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PART III

ON THE BENDING OF A SECTOR OF A CIRCLE

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The author determines in what follows the deflexion of the central plane of a thin elastic plate of the form of the sector of a circle with special vertical angles under certain given distributions of load. The two bounding radii will be taken to be freely supported and the circular boundary either supported or clamped. Prof. Galerkin used entirely different methods for solving the problem of the bending of a sector of a circle (1919, 24).

Case—I

The deflexion of the central plane of a thin circular plate clamped at the edge $r=a$ carrying a load of weight W concentrated at a point O , distant b from the centre is given by

$$w = \frac{W}{8\pi D} \left[-R^3 \log \frac{bR'}{aR} + \frac{1}{2} \left(\frac{b^2}{a^2} R'^2 - R^2 \right) \right] \quad (1)$$

Where R is the distance of any point P of the circular plate, from O and R' is the distance of the same point from the point O' , the inverse of O , with respect to the circle and D has its usual meaning. (Michell 1902)

Suppose now that the load be placed at the point whose polar co-ordinate are (b, α) where $0 < b < a$ and $0 < \alpha < \pi$. Then the deflexion w_1 is given by—

$$w_1 = \frac{W}{8\pi D} \left[-R_1^3 \log \frac{bR_1'}{aR_1} + \frac{1}{2} \left(\frac{b^2}{a^2} R_1'^2 - R_1^2 \right) \right] \quad (2)$$

$$\begin{aligned}\text{Where } R_1^2 &= (x - b \cos \alpha)^2 + (y - b \sin \alpha)^2 \\ R_1'^2 &= (x - b' \cos \alpha)^2 + (y - b' \sin \alpha)^2 \\ b' &= \frac{a^2}{b}.\end{aligned}$$

We now put another load of equal weight at the point $(b, 2\pi - \alpha)$ if w_2 be the corresponding deflexion, we have—

$$w_2 = \frac{W}{8\pi D} \left[-R_2^2 \log \frac{bR_2'}{aR_2} + \frac{1}{2} \left(\frac{b^2}{a^2} R_2'^2 - R_2^2 \right) \right]$$

$$\begin{aligned}\text{Where } R_2^2 &= (x - b \cos \alpha)^2 + (y + b \sin \alpha)^2 \\ \text{and } R_2'^2 &= (x - b' \cos \alpha)^2 + (y + b' \sin \alpha)^2\end{aligned}$$

We now consider the function—

$$w = w_1 - w_2 = \frac{W}{16\pi D} \left[R_1^2 \log \frac{b^2 R_1'^2}{a^2 R_1^2} - R_2^2 \log \frac{b^2 R_2'^2}{a^2 R_2^2} \right] \quad (3)$$

It is easy to shew that $w = \frac{\partial w}{\partial r} = 0$ over $r = a$ and that $\nabla_1^2 w = 0$

every where within the semi-circle $0 < r < a$, $0 < \theta < \pi$ excepting at (b, α) . But if C be a sufficiently small circle round the point the resultant normal thrust round the circumference balances a weight W . It is further easy to shew that $w = 0$ over $\theta = 0$ and $\theta = \pi$. It is also easy to prove that stress $G = 0$ over $\theta = 0$ and $\theta = \pi$. So w as defined by (3) represents the deflexion of the central plane of the semi circular plate $0 \leq r \leq a$, $0 \leq \theta \leq \pi$ under the action of a load of weight W concentrated at the point (b, α) with the circular boundary clamped and the diameter ($\theta = 0$, $\theta = \pi$) merely supported.

Proceeding in the manner indicated above we may shew that the deflexion of a sector of a circle $\left(0 \leq r \leq a, 0 \leq \theta \leq \frac{\pi}{\lambda} \right)$ ($\lambda = 1, 2, 3, \dots$) whose circular boundary is clamped and the bounding radii merely supported carrying a load of weight W concentrated at the point (b, α) where $0 < b < a$ and $0 < \alpha < \frac{\pi}{\lambda}$ is given by,

$$w = - \frac{W}{16\pi D} \left[\sum_{n=0}^{\infty} \frac{2^{\lambda} - 1}{2^{\lambda}} R_n^2 \log \frac{b^2 R_n'^2}{a^2 R_n^2} - \sum_{n=1}^{\infty} R_n^2 \log \frac{b^2 R_n'^2}{a^2 R_n^2} \right] \quad (4)$$

Where

$$\begin{aligned}R_n^2 &= \left\{ x - b \cos \left(\frac{n\pi}{\lambda} + \alpha \right) \right\}^2 + \left\{ y - b \sin \left(\frac{n\pi}{\lambda} + \alpha \right) \right\}^2 \\ R_n'^2 &= \left\{ x - b' \cos \left(\frac{n\pi}{\lambda} + \alpha \right) \right\}^2 + \left\{ y - b' \sin \left(\frac{n\pi}{\lambda} + \alpha \right) \right\}^2\end{aligned}$$

$$\rho_n^2 = \left\{ x - b \cos \left(\frac{n \pi}{2\lambda - 1} - \alpha \right) \right\}^2 + \left\{ y - b \sin \left(\frac{n \pi}{2\lambda - 1} - \alpha \right) \right\}^2$$

$$\rho_n'^2 = \left\{ x - b' \cos \left(\frac{n \pi}{2\lambda - 1} - \alpha \right) \right\}^2 + \left\{ y - b' \sin \left(\frac{n \pi}{2\lambda - 1} - \alpha \right) \right\}^2$$

$$\text{and } b' = \frac{a^2}{b}.$$

Part II

The deflexion of the central plane of a thin circular plate supported along the edge $r = a$, carrying a load of weight W concentrated at the point $(b, 0)$ ($0 < b < a$) may be shewn to be given by the functions, $w^{(s)}$. (This problem was first solved by Fo "ppl. The author had no access to Fo "ppl's work).

$$w^{(s)} = \sum_{n=0}^{\infty} w_n^{(s)} \cos n \theta \quad (s = 1, 2) \quad (5)$$

valid respectively in the regions I and II defined by $b \leq r \leq a$; $0 \leq r \leq b$ including their common boundary.

The functions $w_n^{(s)}$ ($s = 1, 2$) are given by—

$$w_0^{(1)} = A_0^{(1)} + B_0^{(1)} \log r + C_0^{(1)} r^2 + D_0^{(1)} r^2 (\log r - 1) \quad (6)$$

$$w_1^{(1)} = A_1^{(1)} r + B_1^{(1)} r^{-1} + C_1^{(1)} r^3 + D_1^{(1)} r \log r \quad (7)$$

$$w_n^{(1)} = A_n^{(1)} r^n + B_n^{(1)} r^{-n} + C_n^{(1)} r^{n+2} + D_n^{(1)} r^{-n+2} \quad (n = 2, 3, 4, \dots) \quad (8)$$

in region I and by—

$$w_0^{(2)} = A_0^{(2)} + C_0^{(2)} r^2 \quad (9)$$

$$w_1^{(2)} = A_1^{(2)} r + C_1^{(2)} r^3 \quad (10)$$

$$w_n^{(2)} = A_n^{(2)} r^n + C_n^{(2)} r^{n+2} \quad (11)$$

in region II

The values of the constants A, B, C, D are given by—

$$A_0^{(1)} = \frac{W}{16 \pi D} \left[2 a^2 + \frac{1 - \sigma}{1 + \sigma} (a^2 - b^2) - 2 b^2 \log a \right] \quad (12)$$

$$B_0^{(1)} = -\frac{W b^2}{8 \pi D} \quad (13)$$

$$C_0^{(1)} = -\frac{W}{16 \pi D} \left[2 \log a + \frac{1 - \sigma}{1 + \sigma} \left(1 - \frac{b^2}{a^2} \right) \right] \quad (14)$$

$$D_0^{(1)} = \frac{W}{8 \pi D} \quad (15)$$

$$A_0^{(2)} = \frac{W}{16 \pi D} \left[\left(a^2 - b^2 \right) \frac{3 + \sigma}{1 + \sigma} - 2 b^2 \log \frac{a}{b} \right] \quad (16)$$

$$C_0^{(2)} = - \frac{W}{16 \pi D} \left[2 \log \frac{a}{b} + \frac{1 - \sigma}{1 + \sigma} \left(1 - \frac{b^2}{a^2} \right) \right] \quad (17)$$

$$A_1^{(1)} = \frac{Wb}{8 \pi D} \left[2 \log a - \frac{a^2 - b^2}{a^2} \frac{1 + \sigma}{3 + \sigma} \right] \quad (18)$$

$$B_1^{(1)} = - \frac{Wb^3}{16 \pi D} \quad (19)$$

$$C_1^{(1)} = \frac{Wb}{8 \pi D a^2} \left[\frac{b^2}{2a^2} - \frac{1 - \sigma}{3 + \sigma} + \frac{1 + \sigma}{3 + \sigma} \right] \quad (20)$$

$$D_1^{(1)} = - \frac{Wb}{4 \pi D} \quad (21)$$

$$A_1^{(2)} = - \frac{Wb}{8 \pi D} \left[\frac{a^2 - b^2}{a^2} - \frac{1 + \sigma}{2 + \sigma} - 2 \log \frac{a}{b} \right] \quad (22)$$

$$C_1^{(2)} = \frac{W}{8 \pi D} \left[\frac{b^3}{2a^4} - \frac{1 - \sigma}{3 + \sigma} + \frac{b^2}{a^2} \frac{1 + \sigma}{3 + \sigma} - \frac{1}{2b} \right] \quad (23)$$

$$A_n^{(1)} = \frac{W}{8 \pi D} \left[\frac{b^{n+2}}{na^{2n}} - \frac{1 + \sigma}{2n + 1 + \sigma} - \frac{b^n}{(n-1)a^{2n-2}} \frac{3 + \sigma}{2n + 1 + \sigma} \right] \quad (24)$$

$$B_n^{(1)} = - \frac{W}{8 \pi D} \frac{b^{n+2}}{n(n+1)} \quad (25)$$

$$C_n^{(1)} = \frac{W}{8 \pi D} \left[\frac{b^{n+2}}{(n+1)a^{2n+2}} - \frac{1 - \sigma}{2n + 1 + \sigma} + \frac{b^n}{na^{2n}} \frac{1 + \sigma}{2n + 1 + \sigma} \right] \quad (26)$$

$$D_n^{(1)} = \frac{Wb^n}{8 \pi D} \frac{1}{n(n-1)} \quad (27)$$

$$A_n^{(1)} = \frac{W}{8 \pi D} \left[\frac{b^{n+2}}{na^{2n}} - \frac{1 + \sigma}{2n + 1 + \sigma} - \frac{b^n}{(n-1)a^{2n-2}} \frac{3 + \sigma}{2n + 1 + \sigma} + \frac{1}{n(n-1)b^{n-2}} \right] \quad (28)$$

$$C_n^{(2)} = \frac{W}{8 \pi D} \left[\frac{b^{n+2}}{(n+1)a^{2n+2}} - \frac{1 - \sigma}{2n + 1 + \sigma} + \frac{b^n}{na^{2n}} \frac{1 + \sigma}{2n + 1 + \sigma} - \frac{1}{n(n+1)b^n} \right] \quad (29)$$

So, the deflexion of the central plane of the above plate if the load be placed at (b, α) , $0 < b < a$; $0 < \alpha < \pi$ is given

$$\frac{w_1^{(s)}}{w_1} = \sum_{n=0}^{\infty} \omega_n^{(s)} \cos n(\theta - \alpha), \quad (s = 1, 2) \quad (30)$$

Valid in the regions I and II respectively with the same $W_n^{(s)}$ as before.

Now, suppose a load of weight W be placed at the point $r = b$, $\theta = -\alpha$.

Denoting the corresponding deflexion by $\frac{w_2^{(s)}}{w_2}$ we have

$$\frac{w_2^{(s)}}{w_2} = \sum_{n=0}^{\infty} \omega_n^{(s)} \cos n(\theta + \alpha) \quad (s = 1, 2) \quad (31)$$

Now, the function—

$$\begin{aligned} w^{(s)} &= \overline{w_1^{(s)}} - \overline{w_2^{(s)}} \\ &= 2 \sum_{n=0}^{\infty} w_n^{(s)} \sin n \alpha \sin n \theta \quad (s = 1, 2) \end{aligned} \quad (32)$$

may be shewn to represent the deflexion of the central plane of the semicircular plate $0 \leq r \leq a$, $0 \leq \theta \leq \pi$ supported on all its edges carrying a load of weight W concentrated at the point (b, α) .

And in general, we may shew that the function—

$$w^{(s)} = 2^{\lambda+1} \sum_{n=1}^{\infty} \frac{\omega_n^{(s)}}{2^{\lambda n}} \sin 2^{\lambda} n \alpha \sin 2^{\lambda} n \theta \quad (s = 1, 2) \quad (33)$$

(valid in the regions I and II respectively) represents the deflexion of the central plane of the sector of the circular plate ($0 \leq r \leq a$; $0 \leq \theta \leq \frac{\pi}{2^{\lambda}}$) ($\lambda = 0, 1, 2, \dots$) under the action of a load of weight W concentrated at any point (b, α) ($0 < b < a$, $0 < \alpha < \frac{\pi}{2^{\lambda}}$), all the edges being supported.

Region I is given by—

$$b \leq r \leq a, 0 \leq \theta \leq \frac{\pi}{2^{\lambda}} \text{ and Region II is given by—}$$

$$0 \leq r \leq b, 0 \leq \theta \leq \frac{\pi}{2^{\lambda}} \quad (\lambda = 0, 1, 2, \dots)$$

Part III

Let $0 \leq r \leq a$ be a circular plate and let it be supported along the edge carrying a load of weight W spread uniformly along the circular arc $r = b$, $-\alpha < \theta < \alpha$ ($0 < a < \pi$). Then the deflexion of the central plane is given by—

$$w^{(s)} = w_0^{(s)} + \sum_{n=1}^{\infty} \omega_n^{(s)} \frac{\sin n \alpha}{n \alpha} \cos n \theta \quad (34)$$

valid in the two regions I ($b \leq r \leq a$) and II ($0 \leq r \leq b$) where $w_n^{(s)}$ are identical with those occurring in the previous section.

As before, we may now shew that the deflexion of the central plane of the sector of the circle ($0 \leq r \leq a$, $0 \leq \theta \leq \frac{\pi}{2^{\lambda}}$; $\lambda = 0, 1, 2, \dots$) carrying a load of weight W spread uniformly along the circular arc $r = b$, $\beta - \alpha < \theta < \beta + \alpha$

where $o < \beta - \alpha < \beta + \alpha < \frac{\pi}{2\lambda}$ with supported edge is given by the functions—

$$w^{(s)} = 2^{\lambda+1} \sum_{n=1}^{\infty} \frac{w^{(s)}}{2^{\lambda \cdot n}} \frac{\sin 2^{\lambda \cdot n} \alpha}{2^{\lambda \cdot n} \alpha} \sin 2^{\lambda \cdot n} \beta \sin 2^{\lambda \cdot n} \theta \quad (35)$$

($s = 1, 2$)

valid respectively in the regions—

$$(I) \quad b \leq r \leq a, \quad o \leq \theta \leq \frac{\pi}{2\lambda}$$

$$(II) \quad o \leq r \leq b, \quad o \leq \theta \leq \frac{\pi}{2\lambda}$$

Part IV

The deflexion of the central plane of a thin elastic circular plate clamped along the edge $r = a$, under the action of a load of weight W distributed uniformly along the radius $\theta = o$ is given by (1931)

$$\begin{aligned} w_1 = & \frac{W a^2}{2\pi D} \left[\frac{1}{18} \left(\frac{2r^3}{a^3} - 3 \frac{r^2}{a^2} + 1 \right) + \left(\frac{2r^3}{a^3} \log \frac{r}{a} - \frac{r^5}{a^5} + \frac{r}{a} \right) \frac{\cos \theta}{16} \right. \\ & + \left(\frac{r^4}{a^4} - \frac{2r^3}{a^3} + \frac{r^2}{a^2} \right) \frac{\cos 2\theta}{15} + \left(\frac{2r^3}{a^3} \log \frac{a}{r} + \frac{r^5}{a^5} - \frac{r^3}{a^3} \right) \frac{\cos 3\theta}{48} \\ & \left. + \sum_{n=4}^{\infty} \left\{ (n-3) \frac{r^{n+2}}{a^{n+2}} - (n-1) \frac{r^n}{a^n} + 2 \frac{r^3}{a^3} \right\} \frac{\cos n \theta}{(n^2-1)(n^2-9)} \right] \quad (36) \end{aligned}$$

We break up the above series for w_1 into two parts viz.

$$w_1 = u + v$$

where—

$$\begin{aligned} u = & \frac{W a^2}{2\pi D} \left[\frac{1}{18} \left(1 - \frac{3r^2}{a^2} \right) + \left\{ \frac{r}{a} - \frac{r^3}{a^3} \left(1 + 2 \log a \right) \right\} \frac{\cos \theta}{16} \right. \\ & + \left(\frac{r^2}{a^2} + \frac{r^4}{a^4} \right) \frac{\cos 2\theta}{15} + \left\{ \frac{r^3}{a^3} \left(2 \log a - 1 \right) + \frac{r^5}{a^5} \right\} \frac{\cos 3\theta}{48} \\ & \left. + \sum_{n=4}^{\infty} \left\{ (n-3) \frac{r^{n+2}}{a^{n+2}} - (n-1) \frac{r^n}{a^n} \right\} \frac{\cos n \theta}{(n^2-1)(n^2-9)} \right] \quad (37) \end{aligned}$$

and

$$\begin{aligned} v = & \frac{W r^3}{\pi D a} \left[\frac{1}{18} + \left(\log r \right) \frac{\cos \theta}{16} - \frac{\cos 2 \theta}{15} - \left(\log r \right) \frac{\cos 3 \theta}{48} \right. \\ & \left. + \sum_{n=4}^{\infty} \frac{\cos n \theta}{(n^2-1)(n^2-9)} \right] \quad (38) \end{aligned}$$

Contributions to the stresses G, H, N due to u may be proved to be continuous throughout the plate including the boundary $r = a$, excepting at the point $r = a$, $\theta = 0$.

Further, u satisfies the differential equation $\nabla_1^4 u = 0$ throughout $0 < r < a$.

The trigonometric series $f = \sum_{n=4}^{\infty} \frac{\cos n \theta}{(n^2 - 1)(n^2 - 9)}$

is uniformly convergent in θ for all θ .

It therefore represents a continuous function of θ . v as well as contributions to G, H due to v may be shewn to be finite and continuous throughout the plate by ascribing to v and the contributions to G, H due to v for $r = 0$ their corresponding limiting values as r tends to zero.

Now formal differentiation gives—

$$\nabla_1^2 v = \frac{W r}{\pi D a} \left[\frac{1}{2} + \left(4 \log \frac{r}{a} + 3 \right) \frac{\cos \theta}{8} - \sum_{n=2}^{\infty} \frac{\cos n \theta}{n^2 - 1} \right] \quad (39)$$

and since the resulting series is uniformly convergent in θ the sum of the series is the correct expression for $\nabla_1^2 v$.

Now denoting the contribution by v to the normal shearing stress N across a circular arc $r = \text{const}$ by N_1 We have—

$$\begin{aligned} N_1 &= -D \frac{\partial}{\partial r} \nabla_1^2 v \\ &= -\frac{W}{\pi a} \left[\frac{1}{2} + \left(4 \log \frac{r}{a} + 7 \right) \frac{\cos \theta}{8} - \sum_{n=2}^{\infty} \frac{\cos n \theta}{n^2 - 1} \right] \end{aligned} \quad (40)$$

N_1 is thus continuous throughout the plate excepting at the centre.

Again, denoting the contribution of v to the normal shearing stress across a radial element $\theta = \text{const}$ by N_2 we have—

$$\begin{aligned} N_2 &= -D \frac{\partial}{r \partial \theta} \nabla_1^2 v \\ &= \frac{W}{\pi a} \left[\left(4 \log \frac{r}{a} + 3 \right) \frac{\sin \theta}{8} - \frac{1}{2} \left(\frac{1}{n-1} + \frac{1}{n+1} \right) \sin n \theta \right] \end{aligned} \quad (41)$$

The above series is uniformly convergent in the range $\varepsilon_1 \leq \theta \leq 2\pi - \varepsilon_2$ where ε_1 and ε_2 are arbitrarily small positive numbers. This shews that the above series is a correct representation of N_2 at all points of the plate excepting at the centre and along $\theta = 0$.

The formal process of differentiation leads to

$$\nabla_1^2 v = \frac{W}{\pi D a r} \left[\frac{1}{2} + \sum_{n=1}^{\infty} \cos n \theta \right] \quad (42)$$

These series $\sum_{n=1}^{\infty} \cos n \theta$ does not converge. It diverges for $\theta = 0$ or

a multiple of 2π and is summable (C, 1) to the value $-\frac{1}{2}$ for other values of θ .

We therefore take up the curvilinear rectangle—

$$\begin{aligned} r &= r_1, & r &= r_2 \\ \theta &= \gamma, & \theta &= \delta \end{aligned}$$

Where $0 < r_2 < r_1 < a$ and $\gamma < \delta$ ($0 < \delta - \gamma < 2\pi$)

We may prove easily that $\int N ds$ taken along the edges of the above rectangle is equal to

$$-\frac{W(r_1 - r_2)}{\pi a} \left[\frac{1}{2}(\delta - \gamma) + \sum_{n=1}^{\infty} \frac{\sin n\delta - \sin n\gamma}{n} \right] \quad (43)$$

If $0 < \gamma < \delta < 2\pi$, the above rectangle does not contain any part of the line $\theta = 0$ in its interior or on its boundary. And the above value of $\int N ds$ taken along the edges is given by—

$$\int N ds = -\frac{W(r_1 - r_2)}{\pi a} \left[\frac{1}{2}(\delta - \gamma) + \frac{\pi - \delta}{2} - \frac{\pi - \gamma}{2} \right] \quad (44)$$

If however $-\pi < \gamma < 0 < \delta < \pi$ the rectangle contains the part of the line $\theta = 0$ which lies between the circle $r = r_2$ and $r = r_1$, and in this case—

$$\int N ds = -\frac{W(r_1 - r_2)}{a} \quad (45)$$

Also if we take a circle of radius r_3 ($0 < r_3 < a$) the value of $\int N ds$ taken along the entire circumference is equal to $-\frac{W r_3}{a}$.

Since r_1, r_2, r_3 and γ and δ are arbitrary within the limits prescribed above, it follows that a load of weight W is spread uniformly along the radius $\theta = 0$ while the other parts of the circular plate is free from load.

It is easy to verify that $w_1 = \frac{\partial w_1}{\partial r} = 0$ are satisfied over $r = a$

It follows that w , given by formula (36) represents the deflexion of the central plane of a thin circular plate clamped at the edge $r = a$ carrying a load of weight W spread uniformly along the radius $\theta = 0$.

Now, following the plan sketched above we may easily prove that the function

$$\begin{aligned} w &= \frac{W a^3}{\pi D} \left[\left(\frac{2 r^3}{a^3} \log \frac{r}{a} - \frac{r^3}{a^3} + \frac{r}{a} \right) \frac{\sin \alpha \sin \theta}{16} + \left(-\frac{r^4}{a^4} - \frac{2 r^3}{a^3} + \frac{r^2}{a^2} \right) \right. \\ &\quad \left. \frac{\sin 2 \alpha \sin 2 \theta}{15} + \left(\frac{2 r^3}{a^3} \log \frac{a}{r} + \frac{r^5}{a^5} - \frac{r^3}{a^3} \right) \frac{\sin 3 \alpha \sin 3 \theta}{48} \right. \\ &\quad \left. + \sum_{n=4}^{\infty} \left\{ (n-3) \frac{r^{n+2}}{a^{n+2}} - (n-1) \frac{r^n}{a^n} + \frac{2 r^3}{a^3} \right\} \frac{\sin n \alpha \sin n \theta}{(n^2-1)(n^2-9)} \right] \quad (46) \end{aligned}$$

represents the deflexion of the central plane of a thin semi-circular plate $0 \leq r \leq a$; $0 \leq \theta \leq \pi$ clamped along $r = a$ and supported along $\theta = 0$ and $\theta = \pi$, carrying a load of weight W spread uniformly along the radius $\theta = \alpha$ ($0 < \alpha < \pi$).

And finally the deflexion on the sector $0 \leq r \leq a, 0 \leq \theta \leq \frac{\pi}{2\lambda} (\lambda = 1, 2, 3, \dots)$ carrying a load of weight W distributed uniformly along the radius $\theta = \alpha$ ($0 < \theta < \frac{\pi}{2\lambda}$) where the circular boundary $r = a$ is clamped and the bounding radii $\theta = 0, \theta = \frac{\pi}{2\lambda}$ are merely supported is given by—

$$w = \sum_{n=1}^{\infty} \frac{2^{\lambda} W a^2}{\pi D (2^{2\lambda n^2} - 1) (2^{2\lambda n^2} - a)} \left\{ \binom{2\lambda n - 3}{2} \frac{r^{2\lambda n + 2}}{a^{2\lambda n + 2}} - (2^{\lambda n} - 1) \left[\frac{r^{2\lambda n}}{a^{2\lambda n}} + \frac{r^3}{a^3} \right] \right\} \sin 2^{\lambda n} \alpha \sin 2^{\lambda n} \theta \quad (47)$$

I am indebted to Prof. N. M. Basu for his kind interest in the preparation of the paper.

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CHEMICAL INVESTIGATION OF BRYONOPSIS LACINIOSA FRUIT OIL

By

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ABSTRACT

The fixed oil forming 10.2 percent of the fruit of *Bryonopsis laciniosa* contains, palmitic 25.54%, Stearic 19.75%, arachidic 2.8%, and oleic acid 51.9% in mixed acid fraction. The unsaponifiable matter 8.6% of the oil consists of β -sito-sterol, colouring matter and a hydrocarbon.

Bryonopsis laciniosa (Linn.) Naud. (Syn. *Bryonia laciniosa* Linn.) (Vern. gargumaru or shivlingi,) is distributed throughout India from the Himalyas to Ceylon. It is bitter and aperient and is considered to have toxic properties. It is used in the indigenous system of medicine in fevers with flatulence. A bitter principle 'bryonine'¹ has been reported in the plant and no other work on the plant appears to have been done. The fixed oil from the ripe fruits was therefore investigated.

EXPERIMENTAL

The dry ripe fruits procured locally were extracted with petroleum ether (40–60°), a dark viscous oil in 10.2 % yield was obtained which showed the following physico-chemical constants :

Sp. Gr. at 31°C	0.9305
Ref. Index at 21°C	1.4952
Acid value	4.5
Saponification value	189.5
Iodine value (Wij's)	22.3
R. M. Value	0.77
Polenske value	0.4
Unsaponifiable matter	8.6%
Hehner Number	46.6

The oil was saponified and the unsaponifiable matter separated from mixed acids, the acids showed the following chemical constants :

S. V.	199.6
I. V.	25.6

The mixed acids were then separated into solid and liquid acids by modified Twitchell's lead-salt alcohol method.² The percentage and chemical constants of liquid and solid acids are given below :—

	Solid acid fraction	Liquid acid fraction
Yield	11%	89%
S. V.	205.9	212.1
I. V.	6.8	50.8

Quantitative Estimation of Solid Acids Fraction :

The solid acid fraction was converted into methyl esters. 20.19 gm. of the esters were distilled under reduced pressures (5 mm.) with the following results :

	b. range	wt. in grams.
S ₁	165 – 170°	9.273
S ₂	171 – 180°	2.123
S ₃	181 – 190°	2.592
S ₄	above 191°	0.852
S ₅	residue	4.610
	Loss during distillation	0.741

The different fractions obtained were analysed and percentage of various acids in solid acids and mixed fractions were as follows :—

Acids	Percentage in S. acid fraction	Percentage in mixed acid fraction
Palmitic	11.64	1.28
Stearic	52.66	5.79
Arichidic	25.44	2.8
Oleic	10.23	1.12

The fatty acids of each fraction were liberated and a method was sought to identify the acids by use of paper Chromatography. Spiteri's³ partition Chromatography of fatty acids technique with a little modification gave reliable results. It was necessary to use known pure acids as control reference for unavoidable variation in R_f values. However, this is a satisfactory method for rapid identification of individual acids.

Whatman No. 3 paper stripe were impregnated with liquid paraffin in petroleum ether (40–60°) solution (10% w/v). The fatty acids were dissolved in acetone so that 36 mg. of acids were present in 26 ml. of solution and applied to the paper and latter developed with 90% acetic acid. After drying, the Chromatograms were treated with (Ac O)₂ Cu and K₄Fe (CN)₆. The acids appeared as brown red copper complexes. Spiteri used benzene solution for impregnation and reveals the spots by the silver salt method.

Quantitative Estimation of Liquid Acids Fraction :

The estimation of the liquid acids were carried out by two methods, bromination and methyl-ester method.

(a) *Bromination method*—10 gms. of the acids from the liquid acid fraction were estimated by dissolving the acids in dry ether (at -10°C) were brominated according to Jamieson and Boughmann's⁴ modified method. The results are given below :

Acid	Percentage in Liquid Acids	Percentage in Mixed Acids
Oleic	56.5	50.3
Linoleic
Linolenic
Saturated acids	43.5	49.7

(b) *Ethyl-ester method*—The liquid acid fraction was converted into methyl esters. The ester mixture (35.31 gm.) was fractioned under reduced pressure and the results are as follows :—

Fraction	Temp. range	wt. of fraction in gms.
L ₁	155 – 160°	6.230
L ₂	161 – 165°	12.046
L ₃	166 – 170°	4.710
L ₄	171 – 181°	3.836
L ₅	above 181°	2.015
L _r	residue	5.817
Loss during distillation		0.656

Saponification and iodine values of each fraction were determined. The liberated acids from each fraction were Chromatographed by above mentioned technique, and each constituent was identified from the chromatograms. From these values, the amount of various acids in different fractions were calculated. The percentage of each liquid acid fraction and in the mixed acid fraction is given below :—

Acids	Percentage in Liquid Acid Fraction	Percentage in Mixed Acids Fraction
Palmitic	27.26	24.26
Stearic	15.69	13.96
Oleic	57.06	50.78
Linoleic
Linolenic

The total percentage of the various fatty acids in solid, liquid and mixed acids fractions of the *Bryonopsis laciniosa* fruit oil, are as follow :—

Acids	S. Acid Fraction	L. Acid Fraction	M. Acid Fraction
Palmitic	11.64	27.26	25.54
Stearic	52.66	15.69	19.75
Arachidic	25.44	...	2.8
Oleic	10.23	57.06	51.9

The unsaponifiable matter was chromatographed over alumina using petroleum ether (40–60°), benzene and chloroform as eluants. After removal of the solvents from the eluants, the following products were obtained :—

1. White waxy solid m.p. 62–64° soluble in absolute alcohol, methanol, benzene and chloroform. The mixture gave negative Liebermann-Burchard colour reaction. No pure substance could be crystallised out from this.
2. Colourless needles, recrystallised from methyl alcohol m.p. 137–38°. It gave positive Liebermann-Burchard colour reaction. The acetate had m.p. 127–28°. The substance appears to be β -sito sterol.
3. Colouring matter m.p. 205–208° was obtained. This also could not be obtained in crystalline form.

We are very grateful to Dr. I. C. Chopra, Director, Regional Research Laboratory, Jammu, for his valuable advice during the course of this investigation.

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VARIATIONS IN pH AND CONDUCTIVITY OF SOIL BY THE ADDITION OF AMMONIUM CHLORIDE, SODIUM PHOSPHATE AND OIL CAKE

By

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ABSTRACT

The effect of mixing ammonium chloride, sodium phosphate (Na_2HPO_4) and oil cake in soil on pH and conductivity during 180 days of exposure to sunlight has been studied. Initial change in pH and conductivity values of soil suspension are due to the nature and buffering action of the substance added and also due to adsorption of ions. With increasing days of exposure irregular increase in conductivity accompanied by decrease in pH can be explained by the fact that these variations are dependent on various factors like hydrolysis of colloidal complex, adsorption of CO_2 from atmosphere, action of micro-organisms, change in the degree of dispersion and formation of electrolytes as a result of easily soluble salts. A large increase in conductivity may indicate that the soil is favourable to biological activities, there are more water soluble minerals present and therefore, for rapid liberation of plant food.

The pH of a soil dispersed in water is not a simple concept, for the soil particles, which carry ions with them are quite large as compared to molecular dimensions, and these ions, are therefore, not uniformly distributed throughout the solution.¹ The pH of a soil, as measured by shaking in water, depends on the ionic concentration present in it, presence of substances capable of changing their state oxidation or reduction and the carbon di-oxide concentrations in soil air. The conductivity of soil suspension, on the other hand changes with dilution, temperature and period of standing. Thus, investigations based on the determination of pH and conductivity values of soil under changing physical, chemical and biological conditions, present a complex yet interesting aspect of study.

The present communication deals with changes in pH and conductivity values of 1:5 soil suspension by mixing ammonium chloride, sodium phosphate (Na_2HPO_4) and oil cake, during 180 days of exposure to sunlight. Oil cake used in these experiments was "rantil" or niger-seed (*Guizotia Abyssinica*, Cass) oil cake also commonly known in Hindi as "Ramtil", which is commonly cultivated for its seeds from which oil is extracted.

EXPERIMENTAL

A suitable soil sample, obtained from a cultivated field was air dried and coarsely powdered. Oil cake was also powdered and sieved through 100 mesh. Different sets of soil containing 0.5% of each of the above mentioned substances, alone, and in combination, as shown in table 1, were taken in glass jars and regularly exposed to sunlight for about eight hours everyday, for a period of 180 days. The moisture content of the soil in glass jars was kept constant at approximately 20% by the regular addition of distilled water. The mixtures were stirred on alternate days to facilitate aeration. Different soil samples from the glass jars were collected before starting the exposure study and later on after intervals of 30 days.

The soil suspensions were prepared by taking a soil water ratio of 1:5, as adopted by C. S. I. R. Division of Soils, in wide mouthed hard glass bottles and shaking them mechanically for one hour.* These suspensions were made in distilled water which was aerated to bring it in equilibrium with carbon-dioxide of the atmosphere. This was done by bubbling air from outside the laboratory building through it for 24 hours. The conductivity determinations were carried out at $30 \pm 0.05^\circ \text{C}$ in an electrically maintained thermostat using Doran conductivity bridge. The cell constant was determined using N/100 KCl soln and the specific conductivity of all suspensions were calculated. The pH values were measured using Beckman pH meter with glass electrode and calomel as reference electrode.

TABLE 1

Set No.	Composition
1	Soil alone
2	Soil+0.5% ammonium chloride
3	Soil+0.5% sodium phosphate
4	Soil+0.5% ammonium chloride+0.5% sodium phosphate
5	Soil+0.5% oil cake
6	Soil+0.5% ammonium chloride+0.5% oil cake
7	Soil+0.5% sodium phosphate+0.5% oil cake
8	Soil+0.5% ammonium chloride+0.5% sodium phosphate+0.5% oil cake.

TABLE 2

Temp. 30°C .								
Period of exposure in days.	Set 1		Set 2		Set 3		Set. 4	
	Sp. cond. $\times 10^{-5}$ mhos	pH	Sp. cond. $\times 10^{-5}$ mhos	pH	Sp. cond. $\times 10^{-5}$ mhos	pH	Sp. cond. $\times 10^{-5}$ mhos	pH
0	4.815	7.95	185.7	7.35	24.07	8.15	183.6	7.50
30	9.135	8.15	186.7	7.60	15.67	8.25	181.4	7.75
60	0.099	8.00	188.8	7.45	16.53	8.15	183.6	7.55
90	15.18	7.85	188.3	7.35	17.66	8.05	182.4	7.40
120	18.83	7.70	188.8	7.30	21.61	7.90	186.3	7.35
150	21.21	7.75	189.8	7.25	25.18	7.95	188.6	7.30
180	25.30	7.60	190.3	7.20	27.71	7.60	188.6	7.20

TABLE 3

Temp. 30°C.

Period of exposure in days	Set 5		Set 6		Set 7		Set 8	
	Sp. cond. $\times 10^{-5}$ mhos	pH	Sp. cond. $\times 10^{-5}$ mhos	pH	Sp. cond. $\times 10^{-5}$ mhos	pH	Sp. cond. $\times 10^{-5}$ mhos	pH
0	22.70	7.60	188.4	7.40	29.49	7.90	188.5	7.60
30	13.07	8.20	188.4	7.70	19.61	8.20	183.5	7.70
60	14.29	7.90	191.8	7.60	21.21	8.25	188.3	7.50
90	19.69	7.65	190.3	7.35	21.11	8.05	186.3	7.45
120	21.41	7.55	192.3	7.30	20.20	7.95	189.8	7.30
150	23.60	7.40	194.8	7.30	22.99	7.70	194.8	7.30
180	26.92	7.35	198.9	7.20	28.92	7.55	190.8	7.15

DISCUSSION

Results recorded in tables 2 and 3 show variations in pH and conductivity values of soil on the addition of ammonium chloride, sodium phosphate and oil cake. These results can be discussed in two parts.

(i) Changes in pH and conductivity values at zero time i.e. at the starting time.

(ii) Changes during monthly periods.

(i) Variations in conductivity at zero time are due to the change in the concentration of ions in the soil solution brought about by the adsorption of above mentioned substances. NH_4Cl brings about greater change in conductivity than Na_2HPO_4 (sets 2 & 3) which is due to the fact that NH_4Cl being strong electrolyte dissociates to a greater extent than Na_2HPO_4 . Similarly increase in conductivity in set No. 5 on the addition of oil cake is due to the presence of small amounts of nitrogenous, phosphatic, potassic and other water soluble substances in it.

The results at zero time for respective soil treatments can be analysed as follows:—

Conductivity of Soil (Set. 1)	4.8
Cond. of Soil + NH_4Cl (Set. 2)	185.7
Therefore, Cond. of NH_4Cl in soil	180.9
similarly Cond. of Na_2HPO_4 in soil	19.27
„ Cond. of Oil cake in soil	17.90
Cond. of NH_4Cl + Na_2HPO_4 should be (calculated from above data)				205.0
But, Conductivity actually observed is (set 4)	183.6
			Difference	21.4

Similarly, Cond. of soil + NH_4Cl + oil cake should be	...	203.6
Cond. observed (Set. 6.)	188.5
Difference	...	51.1
Calculated Cond. of Na_2HPO_4 + Oil cake	...	42.97
Observed Cond. of Na_2HPO_4 + Oil cake (Set. 7)	...	29.79
Difference	...	12.18
Cal. Cond. of NH_4Cl + Na_2HPO_4 + oil cake	...	222.87
Obs. Cond. of NH_4Cl + Na_2HPO_4 + oil cake	...	188.50
Difference	...	34.27

The above differences in conductivity can be due to buffering action of sodium phosphate and oil cake. They show that NH_4Cl is remarkably buffered by the addition of Na_2HPO_4 and oil cake. Buffering capacity of sodium phosphate is increased in presence of oil cake.

A persual of pH values at zero time shows that by the addition of NH_4Cl the pH is lowered to 7.35 showing acidic reaction of ammonium chloride as well as the fact that it contributes H^+ to the soil. Addition of oil cake with NH_4Cl checks the pH at 7.40 again showing the buffering action of oil cake. Initially high pH in case of Na_2HPO_4 can be attributed to its alkaline nature.

These observations show that adsorption of ions by soil colloids is an important factor during the decomposition of inorganic and organic matter in the soil. Sodium phosphate and oil cake may act as buffers in controlling the pH of the soil. Bhattacharya and Bansal³ also observed the buffering action of oil cake and calculated that an alkali side buffering action of oil cake is better than that of leaves.

(ii) The changes in conductivity and pH values between 30 days and 180 days of exposure to sunlight show that, in general, there is an irregular increase in conductivity as the time increases showing thereby that changes in conductivity are dependent on various factors. During this period soil system enters into various complicated phases. Due to high mobility of H^+ the conductivity should be high when pH is low and *vice versa*. It is seen that though the general trend of readings is that increase in conductivity is accompanied by decrease in pH this is not rigorously true. At certain places decrease in conductivity is accompanied by a decrease or no change in pH and *vice versa*. These results show that changes in pH and conductivity appear to be connected by more than one factor alone.

According to Benade⁴ the factors which influence change in conductivity can be grouped under the following heads :—

- (a) adsorption of CO_2 from the atmosphere,
- (b) action of micro-organisms,
- (c) change in the degree of dispersion of solid phase,
- (d) the formation of simple electrolytes as a result of solution of easily soluble salts and the formation of colloidal electrolytes by the colloidal complex.⁵

Increase in conductivity in set 5 may be the result of bacterial activity, and mineralization of oil cake. Conductivity may increase inspite of low proportions of H ions (i.e., higher pH values), provided mineralization is great. During its decomposition, ammonification and nitrification, oil cake produces certain complex organic acids which decrease the soil pH. CO_2 resulting from the decomposition of organic matter dissolves in water to form carbonic acid as,



and thus the pH of soil system is lowered.

Increase in pH values at 30 days of exposure in set 2 can be due to the presence of basic ammonium ion in the system, but as the oxidation proceeds nitrates are formed, ammonium $\xrightarrow{\text{O}_2}$ nitrite $\xrightarrow{\text{O}_2}$ nitrate. The nitrates formed give rise to nitrous and nitric acids as well as nitrites and nitrates of cations, thus resulting in decrease in pH and increase in conductivity. Moreover, with increase in time NH_4Cl gets hydrolysed and thus contributed H^+ to the soil.

Decrease in conductivity in sets 3, 4, 7 and 8 with sodium phosphate added to the soil after 30 days of exposure to sunlight can be due to the 'fixation' of soluble phosphate because of calcareous natures of the soil. The soluble phosphate reacts with calcium compounds present in the soil resulting in the formation of CaHPO_4 which is probably unstable in soil and reverts to less available forms. Increase in conductivity with time are, thus, due to hydrolysis of calcium phosphate. With increase in days of exposure the pH decreases thereby that more phosphate is joining in to solutions.

It can not be easily said to what extent mechanism of the changes in pH and conductivity is governed by H ion concentration, mineralization of organic matter and the role of microbial populations in soil. It can, however, be reasonably inferred that a large increase in conductivity may indicate that soil is favourable to biological activities, there are more water soluble minerals present into it for rapid liberation of plant food.

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INTAKE OF PHOSPHATE BY HOMOIONIC INDIAN CLAYS

EFFECT OF ASSOCIATING DIVALENT ALKALINE CATIONS WITH KASHMIR BENTONITE

By

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[Received on 12th September 1960.]

ABSTRACT

Phosphate adsorption studies were made with barium, strontium and magnesium derivatives of an Indian montmorillonite (Kashmir bentonite) sample. Four phosphate solutions of different pH were employed. Ba-montmorillonite was observed to remove phosphate from the liquid phase more effectively than either Sr- or Mg-montmorillonite. In view of higher adsorption of phosphate from alkaline phosphates, it has been pointed out that chemical precipitation played a significant role in this process. Such indications were obtained from the non-linearity of the plots between $\log c$ and $\log x/m$ which carry their usual meanings.

INTRODUCTION

In soils, most of the ions are generally associated with the solid phase, a large portion of which constitutes clay minerals. Activities of such substances in relation to their behaviour with the surrounding ions depend to a large extent on the amount and variety of their adsorbed ions, their inherent nature leading to their specificity in structure and the typical deportment of the liquid phase. It is easy to understand that under such circumstances the behaviour of heteroionic minerals with the surrounding cations and anions is hardly within the reach of comprehension and a nearest approach to their behaviour can be made, provided they were studied in homoionic forms. It is natural to conclude that the behaviour of a heteroionic mineral is the total effect of deportment of various cations that it carries and separate studies on the mineral derivatives prepared by each of these cations (homoionic forms) would favourably indicate their total behaviour when associated together with a particular clay. In the present study, adsorption capacities of three derivatives of an Indian montmorillonite (Kashmir bentonite) *viz.*, barium-, strontium- and magnesium-montmorillonites, have been reported and the phase of reaction in which the process would be most favoured with these homoionic clays have been determined. A few years back, Mitra and Prakash (1957) made a somewhat similar study with a different species of Indian montmorillonite.

EXPERIMENTAL

2.5 gm of the derivative minerals (well pulverised) were taken in several 250 ml conical flasks and treated with 100 ml of the phosphate solutions. Then, the mixtures were shaken in a mechanical shaker for an hour, and kept for 48 hours in a thermostat at 30°C. The supernatant liquid was analysed for P_2O_5 content.

The results obtained have been plotted and presented in the graphs to observe the validity of Freundlich's adsorption isotherm rule. The results were originally calculated in terms of mg. of P_2O_5 in 100 ml. solution.

The derivatives were prepared by the method described by Mitra and Prakash (1957).

Description of the curves is given below :

- Curves a.* Adsorption of phosphate ion from $(NH_4)_3 PO_4$
- b.* Adsorption of phosphate ion from $(NH_4)_2 HPO_4$
- c.* Adsorption of phosphate ion from $NH_4 H_2 PO_4$
- d.* Adsorption of phosphate ion from $H_3 PO_4$

DISCUSSION

The following graphs clearly show that the adsorption of phosphate by homoionic Indian montmorillonites considerably depends upon the nature of their exchangeable cations and the reaction of the added phosphate. In all cases, adsorption was favoured in high pH phosphate solution. It is natural to conjecture that the penetration of a cation into the active portion of the mineral changed its

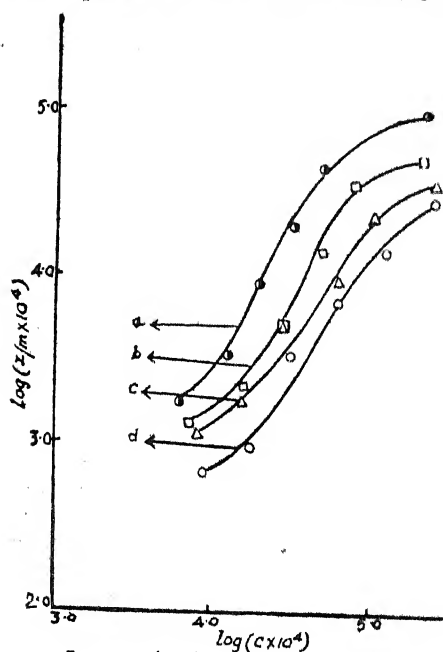


FIG.1 - Adsorption of phosphate ion by Ba-montmorillonite

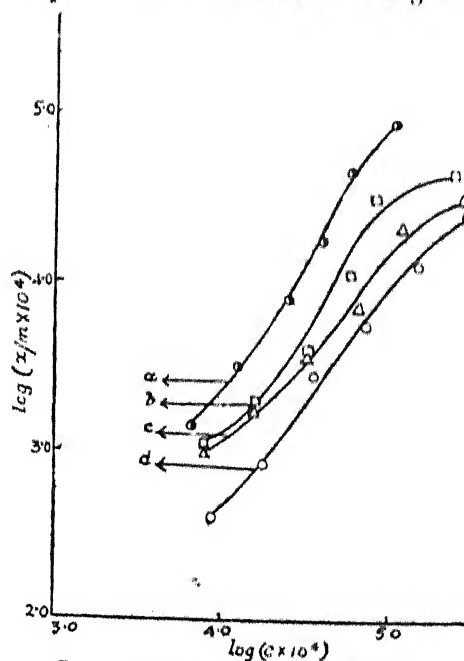


FIG.2 - Adsorption of phosphate ion by Sr-montmorillonite

physico-chemical behaviour with the phosphate solutions employed and the extent of such behaviour was also considerably directed by the amount of a particular cation introduced in the system. In the present investigation, Ba-montmorillonite was observed to remove phosphate more effectively than either Sr- or Mg-montmorillonite.

A perusal of figs. 1 to 3 would show that the plots between $\log c$ and $\log x/m$ which have been used here with their usual meanings, are not linear. Thus, they do not obey Freundlich's adsorption isotherm rule. It may be concluded from the trend of curves observed in these investigations that with these systems, physical adsorption plays a negligible role and the adsorption probably occurs in multi-layers. All curves are typically S-shaped and it is, therefore, undoubted that the mechanism of adsorption is practically identical in all the cases. It may be mentioned here that all the three cations introduced in the active portion of the mineral are known to form insoluble phosphates in a medium of low hydrogen ion concentration. Results reported in the present investigation adequately indicate that such events do occur with Ba-, Sr- and Mg- montmorillonites when they are kept in association with alkaline phosphates.

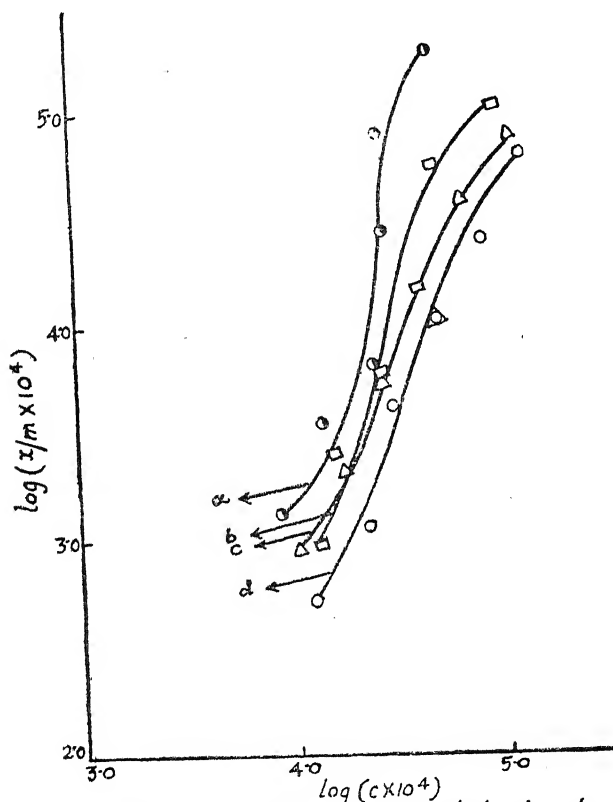


FIG. 3 - Adsorption of phosphate ion by Mg-montmorillonite

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ADSORPTION OF FLUORESCEIN ON HYDROUS MOLYBDIC OXIDE

By

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ABSTRACT

Hydrated molybdic oxide precipitated from a solution of ammonium molybdate with hydrochloric acid has been found to be a good adsorbent for the acidic dye fluorescein. The adsorption isotherms deviate from the ordinary ones and they are S shaped being convex to the concentration axis. This is explained as due to the nature of the dye anions in solutions where they exist in a highly associated state i.e. ionic micellar state. It has been found out that the amount of the dye adsorbed increases both with time and temperature. The results point out that adsorption of fluorescein on hydrous molybdic oxide is mainly chemisorption, possibly preceded by physical adsorption.

Hydrated molybdic oxide precipitated from a solution of ammonium molybdate with hydrochloric acid has been found to be a good adsorbent for the acidic dye Fluorescein. Pelet and Jolivet¹ studied the association of methylene blue with silica. Gyani² showed from his adsorption studies of methylene blue and crystal violet on silica gel that adsorption equilibrium is similar to that obtained in the adsorption of water vapour on solids. Bancroft and Suidas³ made quantitative observations on the adsorption of dyes in presence of cations and anions by hydrous oxide sols. The H^+ ion concentration influences the taking up of dyes by mordants.⁴ Tewari and Ghosh⁵ have clearly shown that the adsorption of Congo Red by hydrous chromium or aluminium oxides depend upon the H^+ ion concentration of the medium in which the oxide is suspended.

Morgan⁶ is of the opinion that the adsorption of dye stuffs as exemplified by aluminium-alizarin lakes is due to the formation of definite metallic chelates. But Biltz and Ackerman⁷ opined the formation of adsorption complexes. Valko⁸ regards adsorption as merely the first step in taking up of a dye by a fibre which is followed in time by the chemical union between the dye molecules and fibre molecules.

In the light of the above controversial ideas it has been thought worthwhile to investigate the adsorption of dyestuffs in its various aspects. Since hydrous molybdic oxide adsorbs to a good extent the dye, Fluorescein, the present communication describes the nature of the adsorption isotherms as also the effect of temperature on the extent of adsorption.

EXPERIMENTAL

The reagents ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and HCl were of E. Merck and C. P. grade quality respectively. The dye, Fluorescein (Soluble), was of B.D.H. quality. A sample of the hydrated oxide of molybdenum was obtained by using 100 c.c. of 0.1M molybdate solution and 24 c.c. of 2.5 N HCl for precipitation. The freshly precipitated oxide is appreciably soluble in water⁹. Hence the precipitate was kept in contact with the mother liquor for a week and then the sample was washed with distilled water till free from adsorbed electrolytes. The precipitate was made into a fine suspension and the molybdenum content was estimated as lead molybdate.

Increasing amounts of the dye solution were added to 25 c.c. of suspension in several 250 c.c. flasks maintained at a temperature of 30°C in a thermostat. After thorough shaking, the total volume was made up to the mark and was kept at the same temperature for another five minutes. A part of the solution was taken out and centrifuged for a constant time *i.e.* 10 minutes in every case and the amount of dye in it was estimated by a Photoelectric Colorimeter (Litchte Liches Kolorimeter, Model VI) using a blue filter and 30 c.c. cuvettes. Since the adsorption of this dye is a slow process, the measurements were made at definite intervals of time, 15 minutes, 30 minutes, 1 hour, 2 and 3 hours, keeping the flasks at the same temperature. Since the original amounts of dye added are known, the amount of the dye adsorbed can be calculated. The results obtained at different temperatures are recorded in the following table, and the adsorption isotherms are shown in Fig. 1.

Amount of molybdic acid present in 25 c.c. suspension = 0.2429 grams. (m).

Strength of dye solution used = 0.02 %.

c = Equilibrium concentration (in mg.).

x = Amount of dye adsorbed (in mg.).

Time of contact - 3 hours

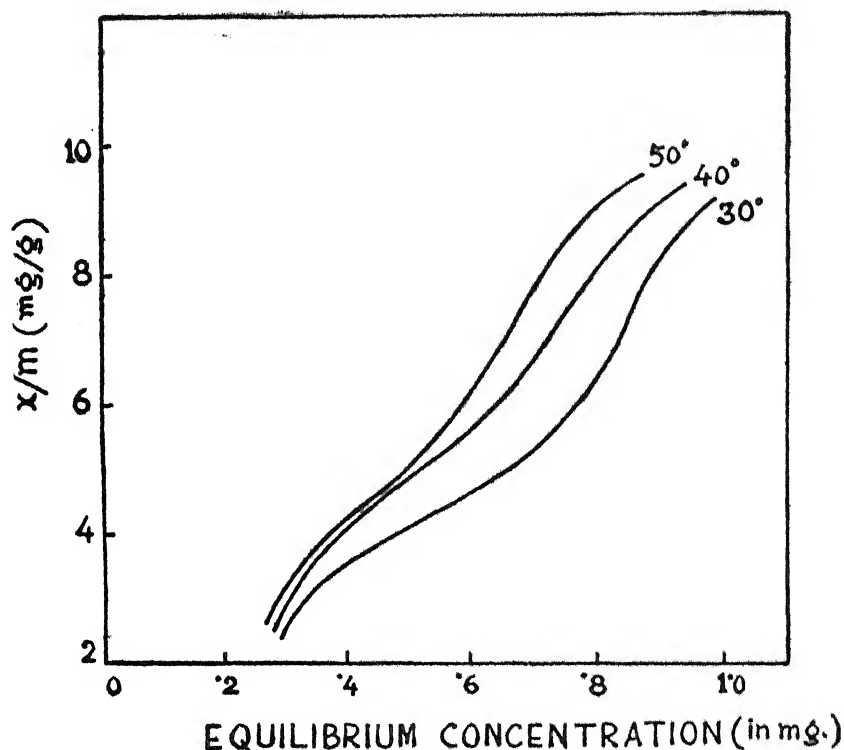
Vol. of dye added (c.c.)	Temperature								
	30°C			40°C			50°C		
	c	x	x/m	c	x	x/m	c	x	x/m
15.0	0.92	2.03	8.567	0.86	2.14	8.810	0.80	2.20	9.057
12.5	0.81	1.69	6.676	0.72	1.78	7.028	0.67	1.83	7.350
10.0	0.70	1.30	5.352	0.60	1.40	5.763	0.57	1.43	5.887
7.5	0.50	1.00	4.117	0.43	1.07	4.406	0.43	1.07	4.406
5.0	0.32	0.68	2.800	0.30	0.70	2.882	0.28	0.72	2.972

DISCUSSION

It was observed that a good amount of adsorption occurs within the first few hours but as much as 2 to 3 days are required for complete equilibrium. The adsorption of Fluorescein is a slow process and increases with time. Similar results have been reported by Yoe¹⁰. From the values of the amount of the dye adsorbed and its

equilibrium concentration after 3 hours contact between the adsorbent and the adsorbate, the adsorption isotherms were drawn. The adsorption curves show

FIG.1 ADSORPTION ISOTHERMS



a deviation from the ordinary adsorption isotherms specially for smaller duration of time. The curves are S shaped being convex to the concentration axis and very similar to the experimental data of Coolidge¹¹ for the adsorption of water vapour by charcoal. Hajela¹² too has obtained similar isotherms in his adsorption studies of crystal violet dye on hydrous chromic oxide. This characteristic form of isotherms has been ascribed by Coolidge to molecular association of polar substance in solution.

Choudhary and Das Gupta¹³ have shown that Eosin and Fluorescein dyes are polar substances behaving as colloidal electrolytes and thus remain in a highly associated form in solution. So, the S shaped curve for the adsorption isotherms obtained in the present case justifies the contention of Coolidge.

Generally adsorption is an exothermic process and so increase in temperature should cause a decrease in adsorption. But it is significant to note from the table that the amount of the dye adsorbed increases with temperature. Similar results have also been reported by Hajela (*loc. cit.*) H. S. Taylor¹⁴, in his *General theory of activation energy in adsorption process* has pointed out the possibility of rising values of adsorption with increasing temperature. The Fluorescein dye is well known to

exist in an aggregated state as already pointed out, and so an increase in temperature may cause the dissociation of the micelle into simpler units resulting in an increase in adsorption. Also the results of experiments on the irreversibility of adsorption, heat of adsorption, slow rate of adsorption, which will form the subject matter of further communications, established the fact that adsorption of Fluorescein on hydrated molybdic oxide is mainly chemisorption, possibly preceded by physical adsorption.

The authors thank Prof. A. K. Bhattacharya, Head, Department of Chemistry, for his keen interest in these investigations. One of the authors (U. V. S.) is indebted to the Government of India for providing a research scholarship.

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A STUDY ON THE ADSORPTIVE BEHAVIOUR OF MONTMORILLONITE AND KAOLINITE CLAYS WITH PHOSPHATES AT DIFFERENT pH VALUES

By

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ABSTRACT

The adsorption of phosphate ions from eight phosphate samples of different pH, by Kashmir bentonite, Wyoming bentonite, Bihar kaolin (Jink Pan) and Georgia kaolin, has been studied at different pH values. It has generally been observed that with both the minerals, the adsorption tends to be greater in cases where the addition of an acid has been made and this tendency gets diminished in the presence of an increased number of hydroxyl ions in the system. Generally, in all cases, phosphate fixation is accompanied by an increase in the resultant pH. On these bases, it has been postulated that the hydroxyl ions are released and the phosphate ions are removed from the solution. Silica/sesquioxide ratio of the minerals was found to be the more important factor influencing the phosphate adsorption process.

INTRODUCTION

Recently, in a detailed study on the adsorptive behaviour of montmorillonite and kaolinite clays with different phosphate ions, De (1) emphasized the complexity in the nature of the mechanism of the process and observed that neither chemical precipitation nor metathetical reactions could alone explain such phenomena. Such conclusions were also reached by a number of other workers (2,3,4,5,6,7,8,9,10). The probability of exchange reactions involving liberation of hydroxyl ions in the system was, however, postulated to be one of the mechanisms through which the phosphate ions were removed from the solution. These exchange reactions were thought to be partly physical and partly chemical in nature, in order to use the term in its broadest possible sense. The explanation that the adsorption phenomenon occurs through exchange of hydroxyl ions was primarily based on the observance of the tendency of the phosphate ions being removed preferentially more from the acid phosphates than from the alkaline ones. The adsorption studies were carried out on the comparative basis and it was observed by De (1) that by performing such investigations with different phosphates and minerals it became easier to indicate the more important factor (silica/sesquioxide ratio) influencing the phosphate adsorption process. In order to get further support on this point it was deemed necessary that the adsorption studies be made at different pH and the changes of pH were noted. The experiments reported here are only for throwing light on the point that the release of hydroxyl ions from the minerals either due purely to exchange reaction or chemical precipitation, evoked in presence of different phosphate solutions, is the outcome of one of the several reactions causing phosphate fixation.

EXPERIMENTAL

Four samples of minerals (Kashmir bentonite, Wyoming bentonite, Bihar kaolin and Georgia kaolin) and eight samples of phosphates (H_3PO_4 , $NH_4H_2PO_4$, NaH_2PO_4 , NH_4NaHPO_4 , Na_2HPO_4 , $(NH_4)_3PO_4$, Na_3PO_4 , and K_3PO_4) were taken for the investigation.

The Indian samples were collected from their respective places and the foreign samples were obtained from Ward's Natural Science Establishment, Inc., U. S. A. For identification, the X-ray analyses of the minerals were originally performed by Late Dr. S. P. Mitra.

The samples of minerals were finely powdered and sieved through a 100 mesh sieve. 2.5 gm. of these minerals were taken in different 250 ml. conical flasks and 90 ml. of aqueous solutions of hydrochloric acid or of sodium hydroxide (of known pH values) were added and were allowed to stand at 30°C for 24 hours. To these, 10 ml. of the phosphate solutions containing 33.8046 milligrams P_2O_5 were added. The flasks were allowed to stand in a thermostat at 30°C for another 24 hours and were occasionally shaken. After the period, 10 ml. of the supernatant liquid were pipetted out. P_2O_5 content was estimated by ammonium phosphomolybdate method. pH determinations were made in the solutions of the duplicates by Leeds Northrup pH meter operated on 22Cv/50 cycles a. c. mains. A glass - calomel electrode system supplied by the same manufacturer was employed. The scale was calibrated with the help of a phthalate buffer before measurements and was checked occasionally.

RESULTS AND DISCUSSION

The results are observed to be somewhat erratic in nature. Nevertheless, appreciable fixation from the phosphate solutions was found, increased tendency of this fixation being more in the presence of an increased hydrogen ion concentration. As the concentration of these ions was reduced, this tendency was considerably diminished and thus, at higher pH the fixation was less than at lower pH. From acid phosphates, also, the fixation was more than from the basic phosphates. Further, the minerals montmorillonites recorded higher fixation than the kaolinites and among themselves the Indian minerals seem to be better adsorbents than the corresponding foreign species used in these investigations.

Bradfield, Scorseth and Steele (11) stated that the fixation of phosphate depends upon three conditions overlapping in nature :—

- (i) At pH 2 to 5 the reaction is due to the gradual formation of iron and aluminium ions and their precipitation as phosphates.
- (ii) At pH 4.5 to 7.5 the phosphate seems to be fixed on the surface of clay minerals.
- (iii) At pH 6 to 10 the phosphate is fixed largely by divalent cations, if present.

Mattson (12) has also drawn the following conclusions from his curves which registered four maxima :—

1. At *very high pH*. The highly insoluble basic phosphate is here precipitated by calcium which in its silicate, carbonate and humate combination is partly displaced by sodium.
2. At *pH 7 to 8*. A less basic neutral or slightly acid phosphate is here precipitated by calcium which in its silicate and carbonate combination is here actively displaced by H^+ ions.
3. At *pH 4*. The PO_4 adsorption (precipitation) due to aluminium begins at much high pH but attains here a maximum as a result of rapid activation of aluminium ions which in their hydroxyl, silicate and humate combination are here actively displaced by H^+ ions.

4. At pH 2. The PO_4 adsorption due to iron begins likewise at a much higher pH but attains here a maximum as a result of rapid activation as in the case of calcium at pH 7 to 8 and aluminium at about pH 4.

In the case of bentonites, a few observations were noted which supported the contention of Scarseth (4) and others that the maximum fixation of phosphates by these minerals usually occurs at pH 6. Similarly, in the case of kaolinites, the maximum fixation was found to occur at pH 4, which diminished towards the alkaline side.

The pH of the solutions used in these investigations varies from 4 to 10; it is, therefore clear that the phosphate fixation has taken place under nearly all conditions prevalent in nature.

It is rather difficult to distinguish between the phosphate adsorption by chemical precipitation and surface adsorption. In view of the complexity in the nature of the phenomenon, it may be pointed out that there is every possibility of an associated role of the factors responsible for adsorption being played in the system. In every case, however, it has been postulated that the hydroxyl ions are released and the phosphate ions are removed from the solution. In the acid range, the pH of the mixture rose, indicating thereby the interactions occurring between the minerals and the phosphate solutions involving also the release of the hydroxyl ions from the solid phase. Some workers believe that the increase of pH of the mixture may also be due to the removal of H^+ ions from the reacting system. The possibility of such an event seems less probable in the present investigation in view of the absence of this tendency in most cases towards the alkaline side. It may, however, be conjectured that the addition of aqueous sodium hydroxide to the minerals caused precipitation of some of the sesquioxide portion of the clays as hydrous oxides of its components, and the adsorption occurred under the influence of their activity. Such precipitates varied in their nature of basicity depending upon the pH of the system (1), and thus the amount of adsorption of phosphates varied accordingly. The reaction of aqueous sodium hydroxide with the minerals causing such precipitations naturally diminished the pH and because of low fixation of phosphate at higher pH, the release of hydroxyl ions as a result of adsorption is not as much as the amount of hydroxyl ions removed from the solution for precipitation. Perhaps because of this break in the balance of the total active hydroxyl ions, the pH of the mixture recorded a low pH in the alkaline range.

Higher fixation from montmorillonite samples has been ascribed to be due to either of the symmetrical structure of the minerals or to their having low silica/sesquioxide ratio. These results are also, in general, supported here.

Further, it is significant that the adsorption from ammonium and sodium phosphates is higher than potassium phosphates. Recently Bottini (13), noted that phosphate bound to H^+ , Na^+ or Ca^+ ions were generally more subjected to fixation than those bound to K^+ . It thus appears that the adsorption of phosphates also depends appreciably on the nature of the cation.

It is, therefore, evident that the reactions responsible for the retention of phosphates by these minerals involve mainly the release of the hydroxyl ions from the solid phase and the removal of the phosphate ions from the surrounding solution.

ACKNOWLEDGEMENTS

The author takes this opportunity of expressing his deep sense of gratitude to Late Dr. S. P. Mitra under whose inspiring guidance the present work was undertaken. He also conveys his deep sense of gratitude and indebtedness to Prof. S. Ghosh and Dr. A. K. Dey, for their kind interest in the problem, valuable suggestions and constructive criticisms.

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CHEMICAL COMPOSITION OF PEGANUM HARMALA SEED OIL

By

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Peganum Harmala Linn. (Vern. Harmala) N. O. Rutaceae, is a tall herbaceous plant which grows throughout India. The seeds are narcotic and are given in fevers and colic and are also used for eradication of tapeworms. In addition to alkaloids¹ the presence of 14.23% oil² is reported but the chemical composition of the oil does not appear to have been worked out.

The crushed seeds on petroleum ether extraction in a Soxhlet gave brownish-yellow oil in 11.1% yield, having following characteristics :—

Specific gravity at 31°C	0.9163
Refractive index at 31°C	1.4723
Acid value	5.3
Saponification value	184.5
Iodine value (Wij's)	120.5
R. M. value	0.77
Polenske value	0.45
Unsaponifiable matter	7.3%

500 gms of the oil was saponified and after removal of the unsaponifiable matter (33.9 gms), the acids were liberated, these showed the following constants :—

Neutralisation value	201.2
Iodine value (Wij's)	127.5

Twichel's Modified lead salt alcohol method³ was applied for splitting the mixed acids into solid acid and liquid acid fractions.

Liquid acids fraction

Percentage	91.8
Neutralisation value	201.3
Iodine value (Wij's)	130.5

95.5 gms. Methyl ester of these on fraction at reduced pressure (5mm) gave the following results :—

Fraction	Boiling range	Weight in gms.
L ₁	166-171°	10.082
L ₂	171-176°	13.173
L ₃	176-180°	13.976
L ₄	180-181°	13.364
L ₅	181-181°	13.361
L ₆	181°-falling	2.145
L ₇	Residue	9.0
Loss during distillation		0.399

The different fractions obtained were analysed⁴ and percentage of various acids in liquid acids and mixed acids fractions were as follows :—

Acids	Percentage in L. acids fractions	Percentage in M. acids fractions
Palmitic	15.2	13.93
Stearic	0.24	0.02
Oleic	43.2	39.65
Linoleic	41.4	38.0

The acids of each fraction were identified with the help of paper chromatography, whatman No. 3 paper strips were impregnated with liquid paraffin in petroleum ether (40°-60°) solution (10% w/v). The fatty acids were dissolved in acetone so that 35 mg. of acids were present in 25 ml. of solution, and applied to the paper and later developed with 90% acetic acid. After drying the chromatograms were treated with $(\text{ACOO})_2\text{Cu}$ (copper acetate) and $\text{K}_4\text{Fe}(\text{CN})_6$. The acids appeared as brown-red copper complexes.

Solid acids fraction

Percentage	8.2
Neutralisation value	201.6
Iodine value (Wij's)	5.2

The quantitative estimation of this fraction was also made by the methyl-ester method.⁴ The dried methyl esters mixture (19.962 gms.) was fractionated

under reduced pressure (5 mm). The results are as follows :—

Fraction	Boiling range	Weight in gms.
S ₁	155-160°	3.189
S ₂	160-170°	3.401
S ₃	170-174°	5.643
S ₄	174-185°	3.517
S ₅	Residue	2.874
Loss during distillation		2.302

On analysing different fractions and identifying the liberated acids with the help of paper chromatography as above the percentage of each in solid acids and mixed acids fractions is given below :—

Acids	Percentage in S. acids fraction	Percentage in M. acids fractions
Oleic	5.8	0.48
Palmitic	48.1	3.94
Stearic	29.54	2.42
Arachidic	8.42	0.69
Behenic	8.21	0.67

The total percentage of the various fatty acids in solid, liquid and mixed acids fractions of *Peganum harmala* seed oil is as follows :—

Acids	S. acids fraction	L. acids fraction	M. acids fraction.
Palmitic	48.1	15.2	17.87
Stearic	29.54	0.24	2.64
Archidic	8.42	—	0.69
Behenic	8.21	—	0.67
Oleic	5.8	43.2	40.13
Linoleic	—	41.4	38.00

Unsaponifiable-matter

The unsaponifiable matter was chromatographed over alumina using petroleum, ether, benzene and chloroform as successive eluants. After removal of the solvents and repeated crystallisation from alcohol, following products were obtained:—

1. White solid (3.2 g) on fractional crystallisations gave two substances (a) m.p. 63-65° and (b) m. p. 79-81°. Both of these gave negative Liebermann Burchard reaction. Substance (a) exhibited violet blue fluorescence in u. v. light. These appear to be some hydrocarbons.

2. White silky needles (23 g) m.p. 139-40°, acetate m.p. 127-28°. Liebermann-Burchard colour reaction in this case was positive. This is B-sito sterol.

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STABILITY OF LYOPHOBIC SOLS

PART V. INFLUENCE OF NON-ELECTROLYTES ON THE ADSORPTION OF IONS BY HYDROUS FERRIC OXIDE SOL.

By

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ABSTRACT

The adsorption of coagulating ion Cl^- from KCl has been measured for positively charged sol of hydrous ferric oxide during its coagulation in presence of various non-electrolytes, viz., ethyl alcohol, acetone, glucose, urea and gelatin. The adsorption of the stabilising ion H^+ has also been determined for a precipitate of hydrous ferric oxide in the presence of the same non electrolytes. It has been observed that there is a diminution of the adsorption of both the stabilising and coagulating ions in the presence of ethyl alcohol and acetone. With glucose and urea there is an increase in the adsorption of both Cl^- and H^+ . With gelatin, there is a decrease of the adsorption of both stabilising and coagulating ions at lower concentration while the reverse is observed at higher concentrations. It is seen that where sensitisation occurs, the adsorption of both the stabilising and coagulating ions decreases whilst for stabilisation this has increased. It is, therefore, concluded that the decrease of the adsorption of either the stabilising or the coagulating ion cannot explain sensitisation or stabilisation.

INTRODUCTION

Weiser³ measured the adsorption of coagulating ions during coagulation of arsenious sulphide, ferric oxide and chromic oxide sols by electrolytes both in the presence and absence of phenol and isoamyl alcohol. He noticed stabilisation of arsenious sulphide sol for BaCl_2 in presence of phenol and the adsorption of Ba^{++} decreased in the presence of the said non-electrolyte. He pointed out that stabilisation was due to the marked cutting down of the adsorption of Ba^{++} by phenol. Mukherjee² could not contribute to this explanation. Choudhury¹ reported that methyl alcohol sensitises arsenious sulphide sol for BaCl_2 while adsorption of Ba^{++} increases at first and then decreases in presence of increasing concentration of alcohol. Here, we have studied the adsorption of both coagulating and stabilising ions in the presence and absence of different non-electrolytes.

EXPERIMENTAL

The hydrous ferric oxide was precipitated from a concentrated solution of ferric chloride by the addition of NH_4OH . The precipitate was thoroughly washed till it was found free from any trace of alkali or acid. A suspension of the precipitate was taken with distilled water to study the adsorption of stabilising ion. A known volume of the suspension with a fixed amount of K_2SO_4 were taken in a series of volumetric flasks. Potassium sulphate was added to prevent colloid formation. Different amounts of HCl were added and the total volume made upto 100 ml. In the corresponding series a known amount of non-electrolyte was also added. The contents were kept overnight and the supernatant liquid was titrated for H^+ .

The precipitate of hydrous ferric oxide was washed till the supernatant liquid was found free from Cl^- . It was peptised by shaking it by a Microid Shaker for about 48 hours with about 0.04 N HCl . A clear brick red sol was obtained which was centrifuged by a Sharple's Super Centrifuge at three speeds namely 6,000 r.p.m., 14,000 r.p.m. and 22,000 r.p.m. to have three samples with different average sized particles. All the samples A, B and C were diluted to contain the same amount of Fe^{+++} /lit. The sol was also used to study the adsorption of the coagulating ion. A known volume of the sol was taken in a series of volumetric flasks and sufficient KCl was added so as to coagulate it in about an hour. The total volume was raised to 100 ml. In the corresponding set a known amount of non-electrolyte was also added. The contents were kept overnight and the supernatant liquid was titrated for Cl^- .

In tables 1 and 2 we give the adsorption of stabilising ion.

Concentration of the suspension = 5.19 gms. Fe_2O_3 /lit.

Volume of the suspension taken = 10 ml.

TABLE 1

Amount added gm. eq. of $\text{H}^+ \times 10^4$	Amount adsorbed gm. eq. of $\text{H}^+ \times 10^4$				
	No non-elec- trolyte	3.0% ethyl alcohol	3.0% acetone	3.0% glucose	3.0% urea
100.0	8.62	8.40	8.40	9.20	9.60
50.0	8.64	8.40	8.50	9.20	9.61
33.3	8.70	8.42	8.40	9.24	9.60
25.0	8.60	8.46	8.44	9.30	9.65
20.0	8.60	8.50	8.50	9.21	9.60

TABLE 2

Amount added gm. eq. of $\text{H}^+ \times 10^4$	Amount adsorbed gm. eq. of $\text{H}^+ \times 10^4$			
	No nonelec- trolyte	0.0001% gela- tin	0.001% gela- tin	0.01% gela- tin
100.0	8.62	8.00	16.40	15.60
50.0	8.64	8.10	16.44	15.54
33.3	8.70	8.00	16.40	15.60
25.0	8.60	8.00	16.46	15.62
20.0	8.60	8.10	16.40	15.60

Concentration of the sol = 6.96 gms. Fe_2O_3 /lit.

Volume of the sol taken = 10 ml.

In tables 3-7, we present the values of the adsorption of coagulating ion.

TABLE 3

Ethyl alcohol %	Amount adsorbed gm. eq. of $\text{Cl}^- \times 10^4$			
	Amount added gm. eq. of $\text{Cl}^- \times 10^4$	Sol A	Sol B	Sol C
0.0	50.0	17.81	20.62	25.80
1.0	50.0	14.86	17.50	22.41
2.0	50.0	14.86	17.48	22.40
3.0	50.0	14.84	17.47	22.36
4.0	50.0	14.82	17.42	22.32
5.0	50.0	14.82	17.41	22.32

TABLE 4

Acetone %	Amount added gm. eq. of $\text{Cl}^- \times 10^4$	Amount adsorbed gm. eq. of $\text{Cl}^- \times 10^4$		
		Sol A	Sol B	Sol C
0.0	50.0	17.81	20.62	25.80
1.0	50.0	8.22	10.91	15.90
2.0	50.0	8.20	10.90	15.90
3.0	50.0	8.21	10.88	15.87
4.0	50.0	8.17	10.82	15.81
5.0	50.0	8.17	10.81	15.81

TABLE 5

Glucose %	Amount added gm. eq. of $\text{Cl}^- \times 10^4$	Amount adsorbed gm. eq. of $\text{Cl}^- \times 10^4$		
		Sol A	Sol B	Sol C
0.0	50.0	17.81	20.62	25.80
1.0	50.0	27.30	30.21	35.60
2.0	50.0	27.32	30.21	35.61
3.0	50.0	27.31	30.32	35.63
4.0	50.0	27.34	30.26	36.64
5.0	50.0	27.34	30.28	35.64

TABLE 6

Urea %	Amount added gm. eq. of $\text{Cl}^- \times 10^4$	Amount adsorbed gm. eq. of $\text{Cl}^- \times 10^4$		
		Sol A	Sol B	Sol C
0.0	50.0	17.81	20.62	25.80
1.0	50.0	37.36	40.20	45.50
2.0	50.0	37.36	40.21	45.50
3.0	50.0	37.37	40.21	45.52
4.0	50.0	37.39	40.22	45.54
5.0	50.0	37.38	40.24	45.51

TABLE 7

gelatin %	Amount added gm. eq. of $\text{Cl}^- \times 10^4$	Amount adsorbed gm. eq. of $\text{Cl}^- \times 10^4$		
		Sol A	Sol B	Sol C
0.0	50.0	17.81	20.62	25.80
0.0001	50.0	7.60	10.31	15.30
0.001	50.0	27.50	30.41	35.01
0.01	50.0	27.46	30.40	35.00

RESULTS AND DISCUSSION

A perusal of the tables 1-7 shows that the adsorption of both the stabilising and coagulating ions decreases in presence of ethyl alcohol and acetone. With glucose and urea the adsorption of both Cl^- and H^+ increases. In presence of small concentrating of gelatin, the adsorption of both the stabilising and coagulating ions decreases whilst at higher concentrations, the adsorptions of both the ions increase.

The adsorption of the coagulating ion is more with the sol containing average finer particles. The decrease or the increase of the adsorption of coagulating ion is, however, more pronounced with finer particles.

Weiser and others³ have pointed that for sensitisation there should be a decrease in the adsorption of stabilising ion or an increase in the adsorption of coagulating ion and for stabilisation the converse should be true. The result, however, show that where sensitisation has been observed the adsorption of both the coagulating and stabilising ions has decreased, whilst for stabilisation this has increased. It is, therefore, not possible to correlate sensitisation or stabilisation with the adsorption of stabilising or coagulating ions.

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STABILITY OF LYOPHOBIC SOLS

PART VI. INFLUENCE OF NON-ELECTROLYTES ON THE ADSORPTION OF IONS BY HYDROUS MANGANESE DIOXIDE SOL

By

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ABSTRACT

The adsorption of the coagulating ion Ag^+ from AgNO_3 has been measured for negatively charged sol of manganese dioxide during its coagulation in presence of various non-electrolytes, viz., ethyl alcohol, acetone, glucose, urea and gelatin. The adsorption of stabilising ion OH^- has, however, been determined for a precipitate of hydrous manganese dioxide in the presence of same non-electrolytes. It has been observed that the adsorption of both the stabilising and coagulating ions decreases in presence of ethyl alcohol and acetone whilst both increase in presence of glucose, urea and gelatin. It is seen that where sensitisation occurs the adsorption of both the stabilising and coagulating ions decreases while for stabilisation this has increased. It is therefore, concluded that the decrease of the adsorption of either the stabilising or the coagulating ion cannot explain sensitisation or stabilisation.

INTRODUCTION

In an earlier communication¹ we noted the adsorption of stabilising and coagulating ions in presence of various non-electrolytes for hydrous ferric oxide. Here we have made similar study for hydrous manganese dioxide.

EXPERIMENTAL

The hydrous manganese dioxide was precipitated from a solution of KMnO_4 by adding an excess of H_2O_2 . The precipitate was thoroughly washed with water till it was found free from any trace of acid or alkali. A suspension of the precipitate in water was used for the study of the adsorption of stabilising ion. 10 ml. of the suspension were taken in a series of volumetric flasks to which different amounts of NaOH were added and the total volume made upto 100 ml. In the corresponding series known amount of non-electrolyte was added. The contents were kept overnight and the supernatant liquid was titrated for OH^- .

A dilute solution of H_2O_2 was added to a solution of KMnO_4 with constant shaking till a dark brown sol of manganese dioxide was obtained which was purified by dialysing for about a week in a cellophane bag. It was then centrifuged at three speeds namely 6,000 r.p.m., 14,000 r.p.m. and 22,000 r.p.m., to have three samples with different average sized particles. All the samples A, B and C were diluted, to contain the same amount of MnO_2 /lit. The sol has been used to study the adsorption of coagulating ion. 10 ml. of the sol with sufficient amount of AgNO_3 was taken in a series of volumetric flasks. The total volume was raised to 100 ml. In the corresponding set a known amount of non-electrolyte was also added. The contents were kept overnight and the supernatant liquid was titrated for Ag^+ .

In the following table the adsorption of stabilising ion are presented,

Concentration of the suspension = 4.608 gm. MnO_2 /lit.

TABLE 1

Amount added gm. eq. of $\text{OH}^- \times 10^4$	No non-electrolyte	Amounts adsorbed gm. eq. of $\text{OH}^- \times 10^4$				
		3.0% ethyl alcohol	3.0% acetone	3.0% glucose	3.0% urea	0.03% gelatin
100.0	12.00	11.51	11.72	14.54	12.92	12.50
50.0	10.20	9.60	9.81	12.61	11.04	10.60
33.3	8.11	7.52	7.74	10.52	8.93	8.51
25.0	6.60	5.90	6.10	8.93	7.33	6.92
20.0	5.62	5.00	5.21	8.00	6.40	6.00

In the tables 2-6, we present the values of adsorption of the coagulating ion Ag^+ .

Concentration of the sol = 5.753 gm. MnO_2 /lit.

TABLE 2

Ethyl alcohol %	Amount added gm. eq. of $\text{Ag}^+ \times 10^3$	Amount adsorbed gm. eq. of $\text{Ag}^+ \times 10^3$		
		Sol A	Sol B	Sol C
0.0	33.3	3.92	6.61	8.77
1.0	33.3	3.55	6.10	8.14
2.0	33.3	3.55	6.11	8.14
3.0	33.3	3.53	6.09	8.13
4.0	33.3	3.54	6.09	8.13
5.0	33.3	3.50	6.04	8.06

TABLE 3

Acetone %	Amount added gm. eq. of $\text{Ag}^+ \times 10^3$	Amount absorbed gm. eq. of $\text{Ag}^+ \times 10^3$		
		Sol A	Sol B	Sol C
0.0	33.3	3.92	6.61	8.77
1.0	33.3	3.15	5.73	7.80
2.0	33.3	3.14	5.74	7.80
3.0	33.3	3.14	5.71	7.72
4.0	33.3	2.96	5.10	7.21
5.0	33.3	2.84	5.00	7.02

TABLE 4

Glucose %	Amount added gm. eq. of $\text{Ag}^+ \times 10^3$	Amount adsorbed gm. eq. of $\text{Ag}^+ \times 10^3$		
		Sol A	Sol B	Sol C
0.0	33.3	3.92	6.61	8.77
1.0	33.3	9.02	11.74	13.96
2.0	33.3	9.02	11.74	13.95
3.0	33.3	9.16	11.81	14.02
4.0	33.3	9.20	11.87	14.10
5.0	33.3	9.40	12.16	14.46

TABLE 5

Urea %	Amount added gm. eq. of $\text{Ag}^+ \times 10^3$	Amount adsorbed gm. eq. of $\text{Ag}^+ \times 10^3$		
		Sol A	Sol B	Sol C
0.0	33.3	3.92	6.61	8.77
1.0	33.3	7.41	10.26	12.48
2.0	33.3	7.40	10.26	12.46
3.0	33.3	7.42	10.29	12.50
4.0	33.3	7.42	10.30	12.52
5.0	33.3	7.46	10.35	12.58

TABLE 6

Gelatin %	Amount added gm. eq. of $\text{Ag}^+ \times 10^3$	Amount adsorbed gm. eq. of $\text{Ag}^+ \times 10^3$		
		Sol A	Sol B	Sol C
0.0	33.3	3.92	6.61	8.77
0.01	33.3	7.81	10.72	12.82
0.02	33.3	8.00	11.04	13.22
0.03	33.3	8.46	11.55	13.80
0.04	33.3	8.67	12.47	13.80
0.05	33.3	8.67	12.49	14.93

RESULTS AND DISCUSSION

It is seen from tables 1-6 that the adsorption of both stabilising and coagulations decreases in the presence of ethyl alcohol and acetone. With glucose, urea and gelatin, however, the adsorption of both the ions increases.

The adsorption of the coagulating ion is more with the sol containing average finer particles. The change of the adsorption of coagulating ion is more pronounced with the finer particles.

Some authors like Weiser² suggested the diminution of adsorption of both the coagulating and stabilising ions by the addition of non-electrolyte. A decrease in the adsorption of stabilising ion or an increase in the adsorption of coagulating ion will result in sensitisation and the reverse will be the case for stabilisation. The results, however, show that where sensitisation has been observed, the adsorption of both the stabilising and coagulating ions has decreased whilst both increase where stabilisation is noticed. It is therefore, not possible to correlate sensitisation or stabilisation with the adsorption of stabilising or coagulating ions.

ACKNOWLEDGMENT

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INTAKE OF PHOSPHATE BY INDIAN MONTMORILLONITE (KASHMIR BENTONITE) IN PRESENCE OF AMMONIUM SALTS

By

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ABSTRACT

Phosphate intake capacity of a sample of Indian montmorillonite (Kashmir bentonite) was studied in presence of ammonium chloride, nitrate and sulphate. All these salts were found to increase phosphate adsorption. In the presence of ammonium chloride, the intake of phosphate was maximum. Minimum adsorption of phosphate was recorded in the presence of ammonium sulphate. Ammonium nitrate was found to take the intermediate position. In all cases, phosphate adsorption was accompanied by an increase in the resultant pH. This has been ascribed to be due to the removal of H_2PO_4^- and HPO_4^{2-} ions formed in the solution at suitable pH and their reaction with hydrous iron oxide and hydrous aluminium oxide surface films and corresponding release of hydroxyl ions. The possibility of exchange between OH^- ions present at the edges and corners of the mineral lattice and the two phosphate ions, has also been referred to. Variations in the extent of phosphate adsorption in the presence of the three ammonium salts has been ascribed to the difference of HH value (ratio of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ions) of the reacting system.

INTRODUCTION

Ammonium sulphate, ammonium nitrate and ammonium chloride have long been used as effective chemicals for the enhancement of soil fertility. It is natural to conjecture that the incorporation of such substances into soil systems considerably direct certain physico-chemical reactions which may or may not be suitable for the growth and development of plants. Phosphorus being the second important member of the trio NPK, the phenomenon of phosphate fixation in soil has drawn much attention of the agricultural chemists; it is one of those reactions that is also believed to be influenced by the addition of ammonium salts. Since variations in the nature of such reactions are also caused by the clay mineral contents of soils, an approach into the actual nature of soil reactions may well be made by investigating the effect of such substances on the intake of phosphate by clay minerals. In the present study, attempts have been directed to observe the effects of three ammonium salts referred to in the beginning on the phenomenon of phosphate retention by one species of Indian montmorillonite viz., Kashmir bentonite. Earlier, Mitra and Prakash (1,2) studied the phosphate intake capacity of this montmorillonite species in detail without any addition of salts.

EXPERIMENTAL

The sample of clay mineral was obtained from Kashmir. X-ray identification of the clay mineral was performed by late Dr. S. P. Mitra. In collaboration with him, Prakash performed the chemical analysis of the clay substance.

The adsorption experiments were carried out as follows :—

2.0 gm. of the mineral (well-pulverised and 100 mesh- sieved) were taken in several 250 ml. conical flasks and to these were added varying amounts of the ammonium salts. 100 ml. of phosphoric acid containing 431.0550 mg of P_2O_5 were then introduced into each of these flasks and were occasionally shaken. The flasks were afterwards allowed to incubate at room temperature ($32^\circ \pm 1^\circ C$) for 24 hours. Next day, the supernatant liquid was carefully analysed for P_2O_5 content by the usual ammonium phosphomolybdate method with certain modifications (3). All pH measurements were made by Leeds Northrup pH meter operated on 220v/50 cycles a. c. mains. A glass- calomel electrode system supplied by the same manufacturer was employed. The calibration of the scale was made with the help of a phthallate buffer before measurements and was checked occasionally. The results reported here are in terms of mg. of P_2O_5 in 100 ml. solution.

Chemical Analysis of Kashmir bentonite (Prakash, 1956)

	Percent
SiO_2	54.560
Al_2O_3	20.500
Fe_2O_3	2.200
P_2O_5	0.013
K_2O	0.624
MgO	5.680
CaO	2.240
Exchangeable (m.e./ 100 gm)	{ Ca 77.20
	{ Mg 28.09
	{ K 1.54
	{ Na Trace

TABLE 1

Variations in pH of H_3PO_4 with the addition of different amounts of NH_4^- salts

Solution (Phosphoric acid + NH_4^- salts)	pH		
	NH_4NO_3	NH_4Cl	$(NH_4)_2SO_4$
H_3PO_4 + 0.5 gm.	4.40	4.2	6.50
H_3PO_4 + 1.0 gm.	4.65	4.45	6.75
H_3PO_4 + 1.5 gm.	4.85	4.70	6.83
H_3PO_4 + 2.0 gm.	5.20	5.05	6.90

TABLE 2

Adsorption of phosphate from H_3PO_4 by Kashmir bentonite

Initial Cone. mg.	Adsorption mg.	Initial pH	pH of the mixture
431.0550	2.8440	3.8	3.85

TABLE 3

Adsorption of phosphate from H_3PO_4 by Kashmir bentonite in presence of NH_4Cl

Reacting mixture (Mineral + H_3PO_4 + NH_4 -salts)	Adsorption mg.	pH of the mixture	Calcium released mg.
1	2	3	4
2.0 gm + H_3PO_4 + 0.5 gm NH_4Cl	155.960	4.55	33.6
2.0 gm + H_3PO_4 + 1.0 gm NH_4Cl	48.513	4.62	26.4
2.0 gm + H_3PO_4 + 1.5 gm NH_4Cl	27.193	4.85	29.4
2.0 gm + H_3PO_4 + 2.0 gm NH_4Cl	21.456	5.10	31.4

TABLE 4

Adsorption of phosphate from H_3PO_4 by Kashmir bentonite in presence of NH_4NO_3

1	2	3	4
2.0 gm + H_3PO_4 + 0.5 gm NH_4NO_3	38.4396	4.60	12.2
2.0 gm + H_3PO_4 + 1.0 gm NH_4NO_3	33.1686	4.75	18.4
2.0 gm + H_3PO_4 + 1.5 gm NH_4NO_3	8.2279	4.88	25.4
2.0 gm + H_3PO_4 + 2.0 gm NH_4NO_3	7.7569	5.24	31.4

TABLE 5

Adsorption of phosphate from H_3PO_4 by Kashmir bentonite in presence of $(\text{NH}_4)_2\text{SO}_4$

1	2	3	4
2.0 gm + H_3PO_4 + 0.5 gm $(\text{NH}_4)_2\text{SO}_4$	7.7250	6.65	21.2
2.0 gm + H_3PO_4 + 1.0 gm $(\text{NH}_4)_2\text{SO}_4$	4.2530	6.80	22.2
2.0 gm + H_3PO_4 + 1.5 gm $(\text{NH}_4)_2\text{SO}_4$	3.0900	6.85	23.2
2.0 gm + H_3PO_4 + 2.0 gm $(\text{NH}_4)_2\text{SO}_4$	2.9987	6.91	25.4

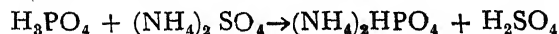
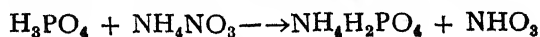
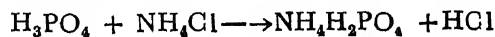
From tables 1 to 5, it is clear that the addition of ammonium salts considerably increases the extent of phosphate adsorption by Kashmir bentonite. In every case, an increase in the resultant pH was noted. The increase has been appreciably influenced by the kind of anion associated with the ammonium radical. Further, increased hydrogen ion concentration in the reacting system has been found to favour increased amount of phosphate adsorption. The ability of the different ammonium salts to enhance phosphate adsorption may be noted to exist in the following order:—



DISCUSSION

In a detailed study on phosphate adsorption by another sample of Kashmir bentonite, De (3) observed the inverse relationship between pH and phosphate uptake. He also noted that in every case, phosphate adsorption brings about an increase in the resultant pH. In the present study however, such inverse relationship has been found when the adsorption studies were carried out in the presence of ammonium salts. Increased adsorption of phosphate was not observed from phosphoric acid the pH of which was lower than any of the solutions used in the present investigations. In all cases, however, phosphate uptake was accompanied by an increase in the resultant pH.

Prakash (4) found with this montmorillonite species increased phosphate fixation from $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ than from H_3PO_4 . The enhancement in the extent of phosphate intake from H_3PO_4 by the present bentonite sample in presence of ammonium salts may, therefore be conjectured to be due to the formation of the following phosphate ions at the suitable pH levels used here :



The H_2PO_4^- and HPO_4^{2-} ions are more easily removed from the solution by the clay mineral sample than H_3PO_4 and there would thus be comparatively lesser quantities of hydrogen ions present in the liquid phase resulting in the increase of the final pH. It is also undoubtedly that these ions reacted with hydrous iron oxide or hydrous aluminium oxide surface films of the mineral and released corresponding

amounts of OH^- ions in the system. De (3) also showed the possibility of exchange between OH^- ions present at the edges and corners of montmorillonite crystal and phosphate ions. It, thus, appears that all these contributed to the increase of the resultant pH.

In general, it may be said that wherever the increase of the final pH was not sufficient, there was lesser amount of phosphate intake. Further, the ratio $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ions (HH) seems to have guided considerably the phenomenon of phosphate adsorption by the clay mineral in presence of ammonium salts. The value of HH would increase with decrease in pH so that in the mixture of phosphoric acid and ammonium chloride there was more H_2PO_4^- than HPO_4^{2-} as the picture was just the reverse in the mixture of phosphoric acid and ammonium sulphate. Prakash (4) has definitely showed with this sample of bentonite that phosphate removal in the form of H_2PO_4^- was greater than in the form of HPO_4^{2-} . Variations in the extent of phosphate adsorption in the presence of ammonium chloride, ammonium nitrate and ammonium sulphate may thus be ascribed to the difference of HH value of the reacting system.

The release of calcium from the mineral has been found to increase with increasing additions of ammonium salts. But with the present data it is not possible to establish any relationship between released calcium and phosphate adsorption.

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MOVEMENT OF MOISTURE UNDER UNSATURATED PHASE

PART II

By

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It is well known that the movement of moisture under unsaturated conditions takes place primarily through capillary forces from surface to surface or in the small pores in the presence of numerous air water interfaces and the dominant force in such movements is the capillary potential.

According to the modern concept the rate of capillary flow of water through soil is given by the equation.

$$Q = - K \text{Grade } 4\psi \quad (1)$$

Where Q = Quantity of water which passes in one second through one square centimeter of an imaginary place perpendicular to the direction of flow.

K = Capillary conductivity.

Grade 4ψ = Capillary potential gradient.

The capillary potential depends upon the soil type, temperature, its compaction and moisture content. If the former factors are fixed, the moisture contents becomes a measure of capillary potential.

\therefore Equation (1) in one dimension becomes

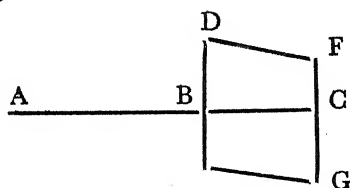
$$Q = - K \frac{dM}{dX} \quad (2)$$

Where M = Moisture content per square centimeter

$\frac{dM}{dX}$ = A measure of force causing the flow.

and X is the horizontal co-ordinate.

Equation of Continuity.



Let ABC be the line of flow and let $AB = X$ and $AC = x + \delta x$.

DEGF may be considered a small volume and the cross-sectional areas of the faces represented by DE and GF may be taken as A where A is very small.

Let the discharge at the face DE at time t be Q per square centimeter.

Total discharge in time δt at the face DE = $AQ \delta t$.

Total discharge in time δt at the face FG = $A \left(Q + \frac{dQ}{dX} \delta x \right) \delta t$.

\therefore Excess of discharge in over the discharge out

$$= AM\delta t - A \left(Q + \frac{dQ}{dX} \delta x \right) \delta t.$$

$$= A \frac{dQ}{dX} \delta x \delta t \quad (3)$$

Original moisture content inside the figure = $M.A. \delta x$.

\therefore Its increase in time $\delta t = \frac{\delta M}{\delta t} \cdot \delta t \cdot A \cdot \delta x$.

\therefore for the equation of continuity = $A \frac{dQ}{dX} \cdot \delta x \delta t = \frac{dM}{\delta t} \cdot \delta t \cdot A \cdot \delta x$.

Dividing by $A\delta X \delta t$ and proceeding to limit

$$\frac{\delta M}{\delta t} = - \frac{dQ}{dx} \quad (4)$$

From (2) and (4)

$$\frac{\delta M}{\delta t} = K \frac{\delta^2 M}{\delta x^2} \quad (5)$$

This question is of the first order in t while it is of the second order in x .

Case I. When it is of the first order

$$\frac{\delta M}{M} = \left(K \frac{d^2}{dx^2} \right) dt.$$

Integrating, $\log M = \left(K \frac{d^2}{dx^2} \right) t + C$.

Where C is arbitrary function of x alone independent of time,

$$\therefore M = e^{Kt \frac{d^2}{dx^2}} \phi(x)$$

Where

putting of $C = \log \phi(x)$

so that $\phi(x)$ is an arbitrary function of x .

Expanding the differential operator, we have

$$\begin{aligned} M &= \left(1 + Kt \cdot \frac{d^2}{dx^2} + \frac{d^4}{dx^4} \dots \frac{K^2 t^2}{2!} + \frac{K^3 t^3}{3!} \cdot \frac{d^6}{dx^6} + \dots \right) \phi(x) \\ &= \phi(x) + Kt \cdot \frac{d^2 \phi}{dx^2} + \frac{K^2 t^2}{2!} \cdot \frac{d^4 \phi}{dx^4} + \frac{K^3 t^3}{3!} \cdot \frac{d^6 \phi}{dx^6} \end{aligned} \quad (6)$$

This contains one arbitrary function $\phi(x)$, as, it should.

From the above equation Dhawan and Malhotra (2) had worked out the ultimate form of

$$K = \frac{1-p}{1-p} \left(\frac{S^2}{t} \right)$$

Case II. When it is of the second order.

Consider the equation

$$\frac{d^2 M}{dx^2} = \mu^2 M \quad (7)$$

Its solution is

$$M = e^{\mu x} A + e^{-\mu x} B$$

Where A and B are independent of x .

Applying this method to (5)

$$M = \frac{x}{e\sqrt{K}} \left(\frac{d}{dt} \right)^{\frac{1}{2}} f(t) + e \frac{-x}{\sqrt{K}} \left(\frac{d}{dt} \right)^{\frac{1}{2}} \psi(t) \quad (8)$$

Where f and ψ are arbitrary functions.

Expanding the operators in (8)

$$\begin{aligned} M = & \left[1 + \frac{x}{\sqrt{x}} \left(\frac{d}{dt} \right)^{\frac{1}{2}} \right. \\ & + \frac{1}{2!} \frac{x^2}{K} \cdot \left(\frac{d}{dt} \right) \\ & + \frac{1}{3!} \frac{x^3}{K^{3/2}} \left(\frac{d}{dt} \right)^{3/2} \\ & + \frac{1}{4!} \frac{x^4}{K^2} \left(\frac{d}{dt} \right)^2 \quad \dots \quad \left. \right] f(t) \\ & + \left[1 - \frac{x}{\sqrt{x}} \left(\frac{d}{dt} \right)^{\frac{1}{2}} + \frac{1}{2!} \cdot \frac{x^2}{K} \left(\frac{d}{dt} \right) \right. \\ & - \frac{1}{3!} \cdot \frac{x^3}{K^{3/2}} \cdot \left(\frac{d}{dt} \right)^{3/2} \\ & + \frac{1}{4!} \cdot \frac{x^4}{K^2} \left(\frac{d}{dt} \right)^2 \quad \dots \quad \left. \right] \psi(t) \end{aligned}$$

$$\begin{aligned} \text{or } M = & \left[f(t) + \psi(t) \right] + \left(\frac{d}{dt} \right)^{\frac{1}{2}} [f - \psi] \frac{x}{\sqrt{x}} \\ & + \left(\frac{d}{dt} \right) [f + \psi] \frac{x^2}{2!K} \end{aligned}$$

$$\begin{aligned}
& + \left(\frac{d}{dt} \right)^{3/2} [f - \psi] \frac{x^3}{3! \cdot K^{3/2}} \\
& + \left(\frac{d}{dt} \right)^2 [f + \psi] \frac{x^4}{4! \cdot K^2} \\
& + \left(\frac{d}{dt} \right)^{5/2} [f - \psi] \frac{x^5}{5! \cdot K^{5/2}} + \dots \dots \dots
\end{aligned}$$

Changing the arbitrary function to $F(t)$ and $\psi(t)$ where

$$F(t) = f(t) + \psi(t)$$

$$\psi(t) = \left(\frac{d}{dt} \right)^{1/2} [f(t) - \psi(t)]$$

We have

$$\begin{aligned}
M = F(t) & + \frac{x^2}{2! K} \cdot \frac{dF}{dt} \\
& + \frac{x^4}{4! K^2} \cdot \frac{d^2 F}{dt^2} + \dots \dots \\
& + \frac{x}{\sqrt{K}} \cdot \psi(t) + \frac{x^3}{3! K^{3/2}} \cdot \frac{d\psi}{dt} \\
& + \frac{x^5}{5! K^{5/2}} \cdot \frac{d^2 \psi}{dt^2} \dots \dots
\end{aligned}$$

This contains two arbitrary functions as it should

At time $t = t_1$

$F(t)$ and $\psi(t)$ are constant and let $x = x_1$

$$Mt_1 = F(t) + \frac{x_1}{\sqrt{K}} \psi(t) \quad (9)$$

Similarly at time $t = t_2$

, $t = t_3$

$$Mt_2 = F(t) + \frac{x_1}{\sqrt{K}} \psi(t) \quad \dots \dots \dots (10)$$

$$Mt_3 = F(t) + \frac{x_1}{\sqrt{K}} \psi(t) \quad \dots \dots \dots (11)$$

From equations No. (9) and (10)

$F(t)$ and $\psi(t)$ are determined

and from (11) we can determine K .

The determination of K with different types of soils under different conditions of compaction, moisture, temperature will reveal clearly the phenomenon of moisture movement under unsaturated conditions, which will ultimately help in solving the intricate problems of soil chemistry, land improvement and soil-mechanics.

SUMMARY

(1) A simple mathematical derivation of the theory of movement of moisture under unsaturated conditions has been investigated.

(2) The determination of K will explain the phenomenon of the movement of moisture under unsaturated conditions and will afford the solution to many knotty problems of soil-physics and soil chemistry.

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MIXED MESOMORPHISM

By

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ABSTRACT

A number of binary systems have been investigated with *p*-azoxyanisole as a liquid crystalline component and another arbitrary normal solute. It is observed that (i) mixed liquid crystals will always be formed over a certain minimum area irrespective of the shape, size and structure of the solute molecules, (ii) dissimilarity in the molecules of the two components causes a difficulty in the packing of the molecules together resulting into a concavity of the transition lines which increases to a minimum with increased mesomorphic tendency of the non-liquid crystalline component and (iii) contribution of the central group towards the mesomorphic tendency of the non-liquid crystalline component seems to be negligible.

A nematic liquid crystal is a system of domain structure in which rod-shaped molecules having translational freedom but restricted rotational freedom, lie parallel in a given domain. Another substance dissolved in such a liquid would be in an anisotropic environment and it would affect the properties of the mesomorphic substance in an interesting manner; the orientation of molecules in a mesomorphic substance will be affected to a more or less extent depending upon the similarity of structure of the dissolved solute. Similar to the depression in melting points by the presence of a foreign substance, the transition points also undergo a depression, the extent of which, depends upon the concentration of another substance mixed with the mesomorphic compound and differs from solute to solute. It is known that on dissolution of another substance in a mesomorphic substance, mixed liquid crystals are formed and as the phenomenon of liquid crystallinity is called mesomorphism, this may be called 'mixed mesomorphism'. Such binary systems of mixed mesomorphism may conveniently be divided into three types viz. (1) where both the components are mesomorphic substances, (2) where one component exhibits mesomorphism and the other is a non-liquid crystal and (3) where both the components are non-liquid crystalline compounds.

A number of binary systems of the types mentioned above were studied by Prins¹, Bogojawlensky and Winogradov², de Kock³, Walter⁴ and others. A more systematic study in recent times, of the second type of binary systems was done by Dave and Dewar^{5,6} who observed very steep transition lines in such systems wherein *p*-azoxyanisole was mixed with substances which should have less tendency to form liquid crystals on fusion. It has also been observed that the transition lines of binary systems, the admixed molecules of which are of dissimilar shape and size have a tendency to show a concavity. During the course of our investigation we have studied the binary systems listed in table 1, comprising of *p*-azoxyanisole as a liquid crystalline component and another arbitrary non-liquid crystalline substance.

The melting points and the transition points alongwith the eutectics of these binary systems are recorded in tables 2 and 3. Values for the slopes of the transition lines of these systems are given in table 4.

TABLE 1

Component A - <i>p</i> -azoxyanisole (a liquid crystal)		
Component B	Mixed with	M. P. °C.
1. Succinic acid		184·0
2. α -Naphthol		94·0
3. β -Naphthol		123·0
4. Benzoic acid		122·0
5. <i>o</i> -Hydroxybenzoic acid		159·0
6. <i>p</i> -Hydroxybenzoic acid		213·0
7. <i>p</i> -Chlorobenzoic acid		236·0
8. <i>p</i> -Toluic acid		179·0

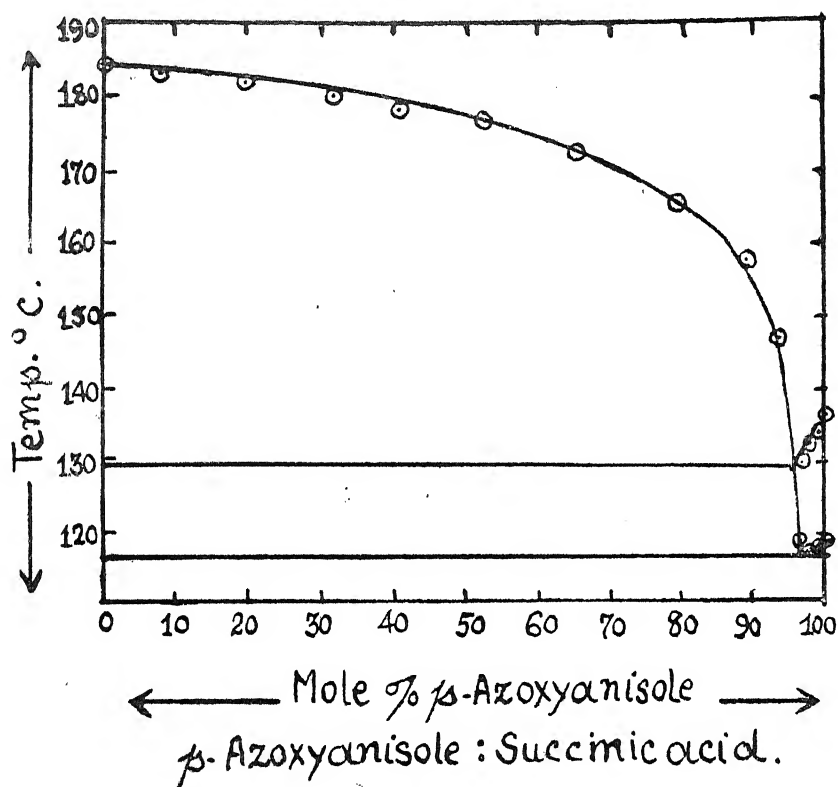


Fig. 1

It can be seen that in the case of system no. 1 (fig. 1), where the non-liquid crystalline component is succinic acid, mixed liquid crystals are certainly

TABLE 2

Solid-liquid transition temperatures for binary systems. The eutectic temperatures and m. p. s. of pure components are direct experimental values : the other temperatures are read from the phase diagrams

No.	0	10	20	30	40	50	60	70	80	90	100	Eutectics	
												Mole % A	Temp. °C.
1.	184.0	183.1	182.4	181.2	179.5	177.5	174.7	170.8	165.2	154.6	118.0	97.0	116.5
2.	94.0	86.7	78.2	66.4	73.8	86.3	96.1	104.0	110.6	115.4	118.0	33.5	60.0
3.	123.0	115.3	106.4	95.5	80.7	89.7	98.0	105.2	111.0	115.5	118.0	39.0	79.8
4.	122.0	115.0	107.7	100.0	94.5	100.8	105.6	109.5	112.7	115.5	118.0	38.2	93.1
5.	159.0	152.5	145.6	138.3	130.5	121.7	111.3	107.4	112.2	115.6	118.0	65.5	104.0
6.	213.0	206.4	199.8	192.7	185.3	177.3	167.5	155.7	138.8	106.0	118.0	88.5	115.0
7.	236.0	228.2	220.2	212.0	203.3	194.2	184.0	171.6	154.2	127.5	118.0	91.5	115.0
8.	179.0	171.0	162.9	154.7	146.0	136.8	126.8	114.6	111.8	114.8	118.0	73.5	109.5

TABLE 3

Amorphous liquid-liquid crystal transition temperatures.

The values are read from phase diagrams.

No.	Mole % of component A														Triple points			
	0	10	20	30	40	50	60	70	80	85	90	93	95	97	99	100	Mole % A	Temp. °C
1.	130.0	134.6	136.0	96.5	129.5
2.	120.5	126.7	133.2	136.0	93.5	116.5
3.	117.3	123.1	128.0	134.0	136.0	92.5	116.0
4.	120.4	124.8	129.7	134.1	136.0	91.0	115.8
5.	117.6	123.3	128.5	134.0	136.0	92.5	116.0
6.	117.7	123.0	126.6	130.4	134.0	136.0	88.5	115.5
7.	124.0	126.5	129.8	134.2	136.0	91.0	122.0
8.	113.5	116.3	120.7	124.4	126.9	130.5	133.3	136.0	72.5	110.5	

formed, but only up to 3.5 mole per cent of succinic acid. Any further addition of succinic acid disturbs the specific orientation of molecules in the mesophase resulting in the complete disappearance of the birefringence. Succinic acid is an aliphatic compound and hence without any benzene rings, at least two of which are considered to be the minimum basic structural requirement of mesomorphism in most of the liquid crystalline substances. However, the disturbing effect caused by succinic acid is limited to a certain minimum. Similarly, α -naphthol and β -naphthol with two benzene rings but much dissimilar in shape and size to *p*-azoxyanisole, have less tendency to form liquid crystals, as is evident from the slopes of the transition lines given in table 4. Even then, mixed mesomorphism is observed up to 6.5 and 7.5 mole per cent of the two naphthols respectively. This indicates that whatever be the structure of the solute molecules and howsoever they may differ in shape and size in relation to the solvent mesomorphic substance, there is a certain minimum limit of disturbance by the solute molecules resulting in a certain minimum area of mixed mesomorphism; in other words, there will always be a minimum certain limit over which mixed liquid crystals will be formed whatever be the shape, size and structure of the solute molecules.

Value for the slope of the transition line in the case of β -naphthol is rather less than that in the case of α -naphthol, indicating a slightly greater tendency of β -naphthol towards mesomorphism than α -naphthol.

Systems 4 to 8 consist of benzoic acids as non-liquid crystalline components. These acids on dimerisation, form linear molecules with two benzene rings, a condition contributory to liquid crystal formation. In a binary system of mixed liquid crystals the nematic-isotropic transition line is a criterion of the liquid crystalline tendency of the non-liquid crystal component. The values of the slopes of the transition lines given in table 4 decrease with the increasing polarity of the end

TABLE 4

No.	Substance	Slope of the transition lines (°C/mole %) $\times 10$
1.	Succinic acid	20.5
2.	α -Naphthol	31.0
3.	β -Naphthol	26.5
4.	Benzoic acid	22.5
5.	<i>o</i> -Hydroxybenzoic acid	27.0
6.	<i>p</i> -Hydroxybenzoic acid	18.0
7.	<i>p</i> -Chlorobenzoic acid	15.5
8.	<i>p</i> -Toluic acid	15.0

groups. Higher the polarity of the end groups, greater is the tendency for liquid crystal formation of the non-liquid crystal component. It can be seen that the value of the ortho-hydroxy substituted acid departs a good deal from that of the

corresponding *p*-hydroxy compound. Gray and Jones⁷ have observed that in a linear nematic liquid crystal, increase in the breadth of a molecule tends to decrease or even destroy mesomorphism. OH group in the ortho position will increase the breadth of the acid molecule and hence will show a lesser tendency towards liquid crystallinity compared to the *p*-hydroxy benzoic acid.

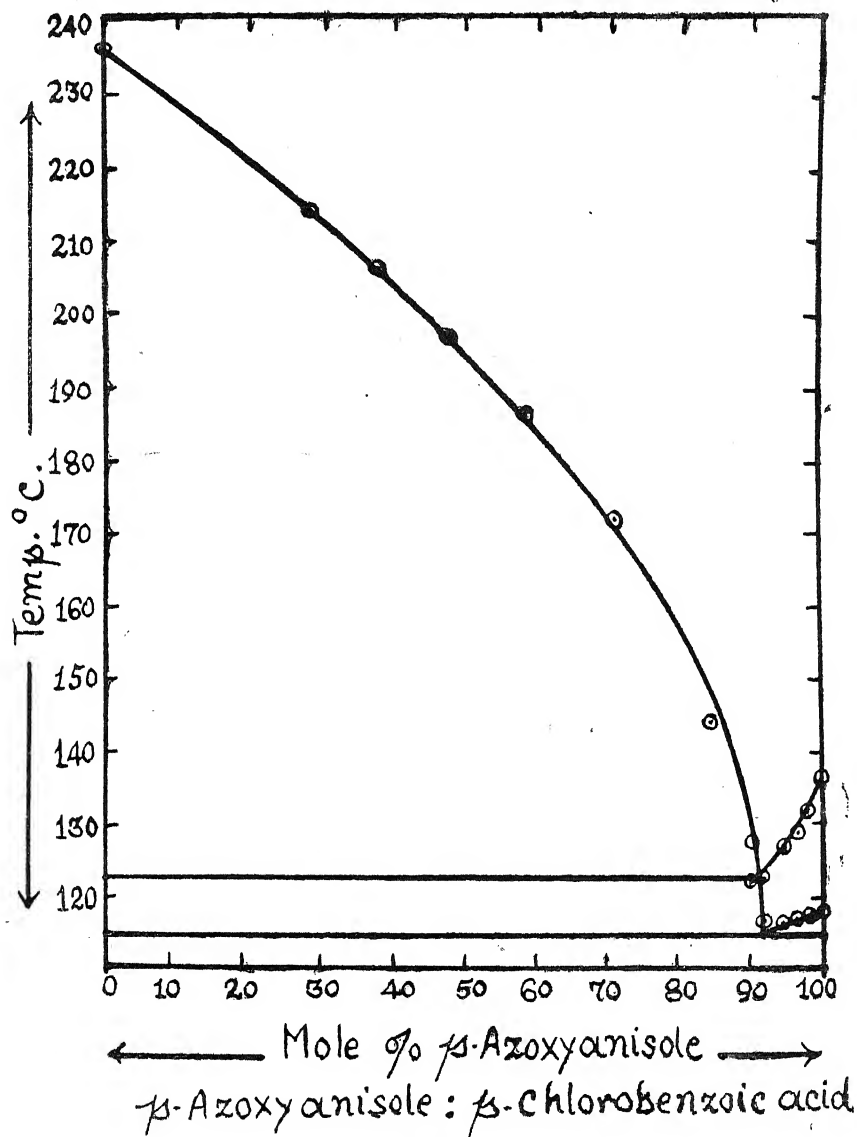


Fig. 2.

A reference to the graphs (figs. 2 and 3) shows that *p*-chloro and *p*-methyl substituted benzoic acids exhibit a concavity in their transition lines. This should

be expected when the molecules of the two components differ in shape and size, due to the difficulty in packing together of the molecules. This concavity should increase and exhibit a minimum in the transition line with the increased mesomorphic tendency of the non-liquid crystal component, which increases with increased polarity of the end groups. Such a minimum in transition line has been observed by Dave and Dewar⁶ in the case of the system *p*-azoxyanisole: anisic acid and by de Kock³ in the system *p*-azoxyanisole: *p*-methoxy cinnamic acid. Our observation in the case of the system *p*-azoxyanisole: *p*-ethoxybenzoic acid is a similar one. This behaviour should be attributed to the dissimilarity in the shapes of the molecules of the two components.

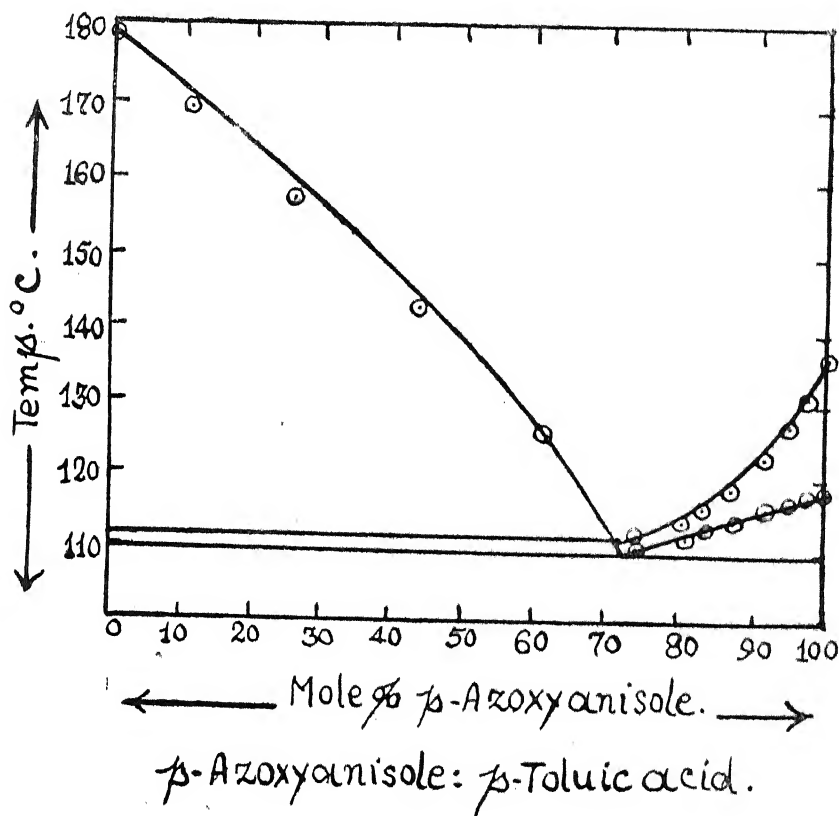


Fig. 3

p-Chlorobenzoic acid and *p*-toluic acid on dimerisation will possess Cl, Cl and CH₃, CH₃ as terminal groups and $\begin{array}{c} \text{O} \cdots \text{H} - \text{O} \\ \diagup \quad \diagdown \\ -\text{C} \quad \text{C}- \\ \diagdown \quad \diagup \\ \text{O} - \text{H} \cdots \text{O} \end{array}$ as the central group. Dave and Dewar⁶ studied the systems *p*-azoxyanisole: *p*-chlorobenzal-*p*-chloroaniline and *p*-azoxyanisole: *p*-tolual-*p*-toluidine, where the schiff's bases have the same Cl, Cl and CH₃, CH₃ end groups but a different central -CH=N-group; they obtained the

values for the slopes of the transition lines as 14.5 for both the systems. A reference to table 4 shows that the systems *p*-azoxyanisole: *p*-chlorobenzoic acid and *p*-azoxyanisole: *p*-toluic acid give comparable values for the slopes of the transition lines. This indicates that in mixed liquid crystal formation, compared to the effect of the end groups, the effect of the central group is either very small or negligible.

EXPERIMENTAL

Purification of the substances :

p-Azoxyanisole was purified by repeated crystallization from alcohol to fine yellow needles. The other non-liquid crystalline substances also were purified by repeated crystallization from suitable solvents like water or dilute alcohol to very fine crystals which melted sharply at their melting points given in literature.

Method of study :

The phase diagrams are studied by the optical method⁵.

SUMMARY

1. Mixed liquid crystals will always be formed over a certain minimum area whatever be the shape, size and structure of the admixed non-liquid crystalline molecules.
2. In mixed liquid crystal formation, whenever the molecules of the components depart from similarity, the transition lines exhibit a concavity which increases to a minimum with increased liquid crystalline tendency of the non-liquid crystalline component.
3. In mixed mesomorphism the effect of the central group of the non-liquid crystalline component seems to be small or negligible.

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ON THE MUTUAL INDEPENDENCE OF A SET OF VARIATES IN MULTIVARIATE ANALYSIS

By

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INTRODUCTION AND SUMMARY

In Section I the mutual independence of the determinant of the dispersion matrix and the ratio of the determinants of two types of the dispersion matrices satisfying Wilks' (Kendall 1951) distribution of dispersion in Multivariate Analysis, has been considered.

In Section II the mutual independence, of the determinant of $n \times$ the second order product moment in the pool of all samples and the determinant of the ratio of the sum of the second order product moment of the samples and the second order product moment in the pool of all samples, has been considered. The generalisation of the results will form the subject of further research.

SECTION I

Let a_{ij} = dispersion matrix $= \sum_{\text{Sample}} \frac{(x_{ik} - \bar{x})(x_{jk} - \bar{x}_j)}{n}$,

$$ij = \frac{\sum x_{ik} x_{jk}}{n}, |a| = \text{determinant } |a_{ij}|$$

and $|a'| = |a'_{ij}|$ Then $|a|$, $|a'|$ satisfy

Wilks distribution (Kendall 1951)

Lemma 1. $E(X^r Y^s) = E(X^r) E(Y^s)$

for every non-negative integers r, s Where $X = |a|$, $Y = \frac{|a|}{|a'|}$

$$\text{Now } E \left\{ |a'|^r \frac{|a|^s}{|a'|^s} \right\} = E \left\{ |a'|^{r-s} |a|^s \right\} = \frac{1}{|B|^r} \prod_{k=1}^p$$

$$\frac{\Gamma\{\frac{1}{2}(n+1-k)+r\}}{\Gamma\{\frac{1}{2}(n+1-k)\}} \prod_{k=1}^p \frac{\Gamma\{\frac{1}{2}(n+1-k)\}}{\Gamma\{\frac{1}{2}(n-k)\}} \times \frac{\Gamma\{\frac{1}{2}(n-k)+s\}}{\Gamma\{\frac{1}{2}(n+1-k)+s\}}$$

$$= E \left\{ |a'|^r \right\} E \left\{ \frac{|a|^s}{|a'|^s} \right\} = E(X^r) E(Y^s)$$

Hence we have

Theorem 1. $|a'|$ and $\frac{|a|}{|a'|}$ are mutually independent.

Proof:—The characteristic function of the joint distribution of X, Y is

$$\begin{aligned}\phi(t_1, t_2) &= \sum_{q=0}^{\alpha} \frac{i^q}{|q|} E(t_1 X + t_2 Y)^q \\ &= \sum_{q=0}^{\alpha} \frac{i^q}{|q|} \sum_{s=0}^{\alpha} \frac{|q|}{|s| |q-s|} t_1^{q-s} t_2^s E(X^{q-s} Y^s) \\ &= \sum_{q=0}^{\alpha} \sum_{s=0}^q \frac{(i t_1)^{q-s}}{|q-s|} E(X^{q-s}) \frac{(i t_2)^s}{|s|} E(Y^s) \\ &= \sum_{a'=0}^{\alpha} \frac{(i t_1)^{q'}}{|q'|} E(X^{q'}) \sum_{s=0}^{\alpha} \frac{(i t_2)^s}{|s|} E(Y^s) = \phi(t_1, 0) \phi(0, t_2)\end{aligned}$$

Hence we have the result.

SECTION II

Let there be a set of K samples of sizes n_1, n_2, \dots, n_k from a p variate normal population.

Let $\bar{X}_i(l)$ be the mean of i th variate in the l th sample.

$$\text{Then } b_{ij}(l) = \sum_{t=1}^{n_l} \{x_{it}(l) - \bar{x}_i(l)\} \{x_{jt}(l) - \bar{x}_j(l)\}$$

n_l is second order product moment in the l th sample

$$\text{Let } \bar{b}_{ij} = \sum_{l=1}^k b_{ij}(l)$$

$$\text{Let } b_{ij} = \sum_t \sum_l \{x_{it}(l) - \bar{x}_i\} \{x_{jt}(l) - \bar{x}_j\}$$

$=$ second order product moment in the pool of all samples.

Kendall (1951) showed that r th moment of the distribution of b_{ij} is

$$\mu_r \{ |b_{ij}| \} = \frac{n^{pr}}{|B|^r} \sum_{m=1}^p \frac{\Gamma\{\frac{1}{2}(n-m)+r\}}{\Gamma\{\frac{1}{2}(n-m)\}}$$

where $|B| = |B^{ij}| = \frac{n}{2} |A^{ij}|$ and $|A^{ij}|$ is

reciprocal to correlation determinant $|l_{ij}|$

Kendall showed that each $b_{ij}(1)$ is distributed in Wisharts' form.

Then the distribution of $b_{ij}(1)$ is given by

$$dF = \frac{|B| \frac{n_l - 1}{2} |b''| \frac{n_l - p - 2}{2} e^{-B^{ij} b_{ij}(l)}}{\prod_{m=1}^p \frac{p(p-1)}{4} \prod_{m=1}^p \Gamma\left\{\frac{1}{2}(n_l - m)\right\}} db''$$

where $|b''| = |b_{ij}(l)|$

Then the characteristic function of the distribution of $b'' s'$ is

$$\int \frac{|B| \frac{n_l - 1}{2} |b''| \frac{n_l - p - 2}{2} e^{-B^{ij} b_{ij}(l) + i t_{ij} b_{ij}(l)}}{\prod_{m=1}^p \frac{p(p-1)}{4} \prod_{m=1}^p \Gamma\left\{\frac{1}{2}(n_l - m)\right\}} \pi db''$$

$$= |B| \frac{n_l - 1}{2}$$

$$\begin{vmatrix} B^{11} - i t_{11} & \dots & \dots \\ B^{1p} - i t_{1p} & \dots & \dots \\ B^{pp} - i t_{pp} & \dots & \dots \end{vmatrix} \frac{n_l - 1}{2}$$

by Siegal's lemma (AITKEN 1949)

Hence the characteristic function of $\overline{b_{ij}}$ is

$$|B| \frac{n - k}{2}$$

$$\begin{vmatrix} B^{11} - i t_{11} & \dots & \dots \\ B^{1p} - i t_{1p} & \dots & \dots \\ B^{pp} - i t_{pp} & \dots & \dots \end{vmatrix} \frac{n - k}{2}$$

if $|B|$ is the same for each of K samples.

Hence the distribution of \overline{b} is given by

$$dF = \frac{|B| \frac{n - k}{2} |\overline{b}| \frac{n - k - p - 1}{2} e^{-B^{ij} \overline{b}_{ij}} \pi dt}{\prod_{m=1}^p \frac{p(p-1)}{4} \prod_{m=1}^p \Gamma\left\{\frac{1}{2}(n - m + 1 - k)\right\}}$$

Where $|\overline{b}| = |\overline{b}_{ij}|$

Now $b_{ij} = \bar{b}_{ij} + m_{ij}$

$$\text{Where } m_{ij} = \sum_{t=1}^k n_l \{ \bar{x}_i(l) - \bar{x}_i \} \{ \bar{x}_j(l) - \bar{x}_j \}$$

Hence the joint distribution will be given by

$$dF = |B| \frac{n-k}{2} | \bar{b} | \frac{n-k-p-1}{2} e^{-B^{ij}} \frac{b_{ij}}{\Gamma(1)} d\bar{b} dF_1$$

$$\frac{\prod_{m=1}^p \frac{p(p-1)}{4}}{\prod_{m=1}^p \Gamma\left\{\frac{1}{2}(n-m+1-k)\right\}}$$

Where dF_1 is the distribution of m_{ij}

$$\text{Hence } \mu'_{r,s} \left\{ | \bar{b}_{ij} | \quad | b_{ij} | \right\} = E \left\{ | \bar{b}_{ij} |^r | b_{ij} |^s \right\}$$

$$= \frac{n^p r}{|B|^r} \prod_{m=1}^p \frac{\Gamma\left\{\frac{1}{2}(n-m-k+1)+r\right\}}{\Gamma\left\{\frac{1}{2}(n-m-k+1)\right\}} \mu'_s \left\{ | b_i | \right\}$$

$n+2r$
for n
in μ'_s

$$= \frac{n^p (r+s)}{|B|^{s+r}} \prod_{m=1}^p \frac{\Gamma\left\{\frac{1}{2}(n-m-k+1)+r\right\}}{\Gamma\left\{\frac{1}{2}(n-m-k+1)\right\}} \times$$

$$\frac{\Gamma\left\{\frac{1}{2}(n-m)+r+s\right\}}{\Gamma\left\{\frac{1}{2}(n-m)+r\right\}}$$

provided the argument of every Gamma function is positive. I am indebted to Dr. M. H. Quenouille for this argument.

This result has been given by Wilks without proof (Wilks Mathematical Statistics P. 24)

Putting $s = -r$

$$\text{We have } \mu_r \left\{ \frac{| \bar{b}_{ij} |}{| b_{ij} |} \right\}$$

$$= \prod_{m=1}^p \frac{\Gamma\left\{\frac{1}{2}(n-m)\right\}}{\Gamma\left\{\frac{1}{2}(n-m)+r\right\}} + \frac{\Gamma\left\{\frac{1}{2}(n-m-k+1)+r\right\}}{\Gamma\left\{\frac{1}{2}(n-m-k+1)\right\}}$$

The criterion for testing the significance of the set of means is defined by

$$F = \frac{| \bar{b}_{ij} |}{| b_{ij} |}$$

Lemma 2 $E(X^r Y^s) = E(X^r) E(Y^s)$

for every non-negative integer r or s

Where $X = |b_{ij}|$ and $Y = |$

$$\begin{aligned} \text{Now } E(X^r Y^s) &= E\left\{ |b_{ij}|^{r+s} \right\} \\ &= \frac{n^p}{|B|^r} \prod_{m=1}^p \frac{\Gamma\left\{\frac{1}{2}(n-m)+r\right\}}{\Gamma\left\{\frac{1}{2}(n-m)+s\right\}} \times \frac{\Gamma\left\{\frac{1}{2}(n-m+1-k)+s\right\}}{\Gamma\left\{\frac{1}{2}(n-m+1-k)\right\}} \\ &= \frac{n^p}{|B|^r} \prod_{m=1}^p \frac{\Gamma\left\{\frac{1}{2}(n-m)+r\right\}}{\Gamma\left\{\frac{1}{2}(n-m)\right\}} \times \prod_{m=1}^p \frac{\Gamma\left\{\frac{1}{2}(n-m)\right\} \Gamma\left\{\frac{1}{2}(n-m+1-k)+s\right\}}{\Gamma\left\{\frac{1}{2}(n-m)+s\right\} \Gamma\left\{\frac{1}{2}(n-m+1-k)\right\}} \\ &= E\left\{ |b_{ij}|^r \right\} E\left\{ \left| \frac{\bar{b}_{ij}}{b_{ij}} \right|^s \right\} = E(X^r) E(Y^s) \end{aligned}$$

Theorem 2. $|b_{ij}|$ and $L = \left| \frac{\bar{b}_{ij}}{b_{ij}} \right|$ are mutually independent,

Proceeding as Theorem 1 we get Theorem 2.

Which may be stated as follows :

The determinant of $n \times n$ second order product moment in the pool of all samples and the determinant of the ratio of the sum of the second order product moment of the samples and the second order product moment in the pool of all samples are statistically independent or independent in the probability sense.

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POLAROGRAPHY OF THORIUM. I

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ABSTRACT

Polarography of thorium has been studied using thorium nitrate. Lithium sulphate has been used as supporting electrolyte in all investigations. A catalytic hydrogen reduction wave is obtained in the region of -1.5 volts. The limiting current is not very reproducible and the limiting current region becomes irregular at concentrations higher than 1×10^{-4} M thorium nitrate. The magnitude of current decreases on increasing the concentration of the supporting electrolyte (lithium sulphate). It has also been observed that thorium ions increase hydrogen overvoltage.

It has been reported that thorium is not determinable polarographically,¹ as its estimated reduction potential is too negative and the hydrolysis of its salts too great, to permit reduction wave, before the reduction of hydrogen ion.² However, some investigators have reported, that they could get reduction wave of thorium in presence of potassium nitrate³ and lithium chloride.⁴

Patterson and Banks⁵ first observed a catalytic wave of thorium in 0.1M potassium chloride in presence of excess nitrate. Recently Masck^{6,7} has studied the depolarizing action of thorium ions in buffered, aqueous and aqueous-alcoholic solutions and has indicated that a reduction wave is observed which is not due to the reduction of thorium ions but involves the reduction of hydrogen ions from the aquo-thorium complex.

Effect of thorium on the reduction waves of certain organic substances have also been observed.⁶

The authors have studied polarography of thorium ions in presence of lithium sulphate as supporting electrolyte. The observations obtained therein have indicated that thorium gives a catalytic reduction wave in this medium and that this wave is not diffusion controlled. It also does not vary linearly with concentration. The effect of varying the concentration of supporting electrolyte has also been studied.

MATERIALS

Thorium nitrate was Shering-Kahlbaum A. G. product. Its stock solution was estimated for thorium content by precipitating it as thorium oxalate and then weighing it as thoria after igniting the oxalate at 1000°C.⁸

Lithium sulphate was Sterling Chemical reagent 99% pure.

Mercury used in the dropping mercury electrode was first purified by chemical treatment and then distilled twice.

EXPERIMENTAL

A Leeds and Northrup Chemograph Type-E was used in all the polarographic estimations. A manual set up was also used whose circuit was similar to the one described by Lingane and Kolthoff⁹.

Current-voltage curves have been taken at room temperature which varied from 30.5°C to 31.5°C. The dropping mercury electrode was used as indicator electrode. All potentials were measured against a Hume and Harris saturated calomel electrode¹⁰ which was used as reference electrode in all experiments.

The characteristics of the dropping mercury electrode used were :—

$$m = 1.6 \text{ mg sec.}^{-1} ; t = 4.68 \text{ sec.} ; m^{2/3} t^{1/6} = 1.769 \text{ mg.}^{2/3} \text{ sec.}^{1/6} ; h = 50 \text{ cm.}$$

pH of the solutions was measured with a Leeds and Northrup pH meter, using general purpose glass electrode.

RESULTS AND DISCUSSION

Experiments were carried out in varying concentrations of lithium sulphate as supporting electrolyte. During experiments the concentration of thorium ions was varied between $5 \times 10^{-5} \text{ M}$ and 10^{-3} M . A reduction wave, appeared in presence of $1 \times 10^{-4} \text{ M}$ or less concentration of thorium ions. At higher concentrations the wave became irregular with ill defined limiting current region. The wave appeared in the region of -1.5 volts. There was no indication of any other wave at more positive potentials.

The half wave potential ($E_{1/2}$) values of reduction waves obtained at different concentrations of lithium sulphate and thorium ions are given in table 1.

TABLE 1
Half wave potential values of the catalytic wave of thorium.

Concentration of thorium nitrate ($\text{M} \times 10^3$)	Concentration of lithium sulphate	$E_{1/2}$
0.05	0.1M	-1.62
0.10	0.1M	-1.63 ₆
0.53	0.1M	-1.66 ₆
1.06	0.1M	-1.65 ₂
0.10	0.05M	-1.56 ₈

The limiting current was tested for diffusion control at concentration $5 \times 10^{-5} \text{ M}$. The values of limiting current at varying heights of mercury column are given below :—

TABLE 2
Limiting current of thorium at different heights of mercury column.

Height of mercury (h) in cm.	Limiting current (i_l) at -1.8 volts in μA	i_l/\sqrt{h}
55	0.424	0.057
50	0.384	0.054
45	0.381	0.056
40	0.375	0.059
35	0.342	0.058
30	0.324	0.059

The above observations show that the current is not solely controlled by diffusion factor.

The limiting current of the reduction wave was measured in presence of differing concentrations of thorium ions. As indicated earlier, the wave became ill defined at concentrations higher than 1×10^{-4} M thorium nitrate. The observations are tabulated in table 3.

TABLE 3

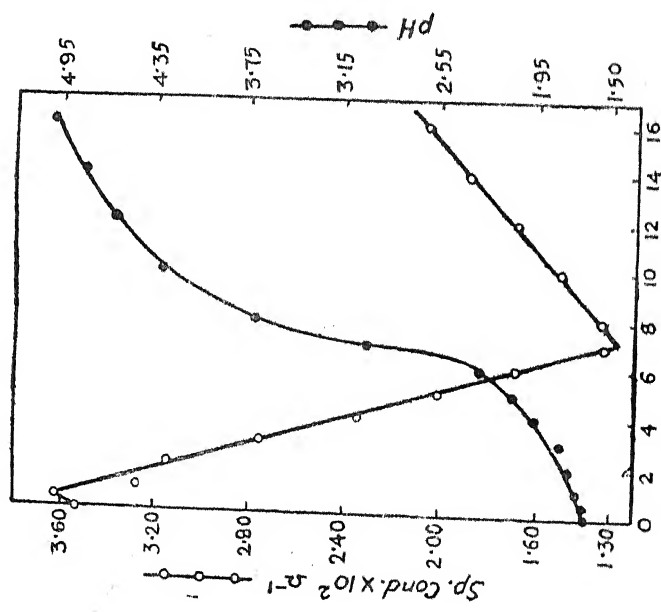
Concentration of thorium nitrate ($M \times 10^3$)	Concentration of lithium sulphate	i_1 at -1.85 volts in μA	$i_1/(M \times 10^3)$
0.05	0.1M	0.384	7.68
0.1	0.1M	0.873	8.73
0.53	0.1M	7.39	13.9
1.06	0.1M	13.135	12.36
0.10	0.5M	0.41	4.1
0.10	0.05M	1.095	10.95

On closer examination of the current-voltage curves, it was observed that the shape of the curve was not very reproducible. The values of limiting currents were not found to be constant at a particular voltage, when the experiments were repeated. In Table 4, some repeated observations are included to show the limit of variation in the limiting current.

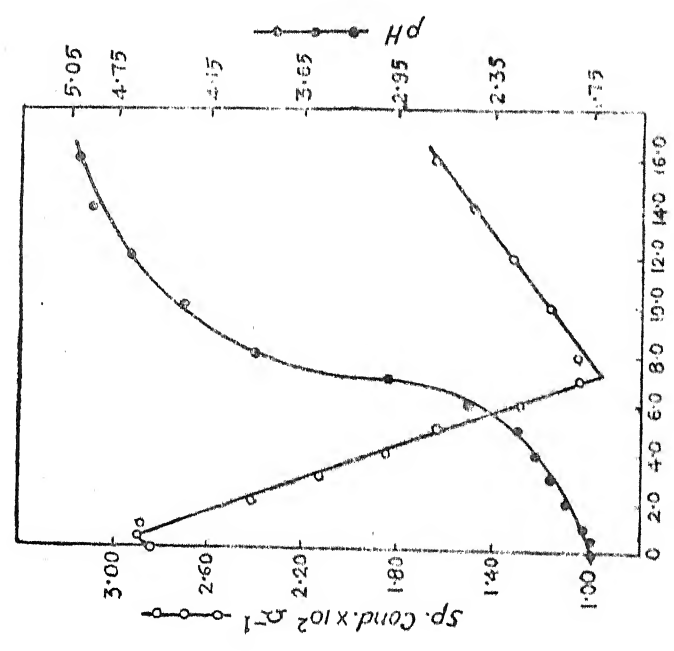
TABLE 4

Concentration of lithium sulphate	Concentration of thorium $M \times 10^3$	Voltage	Current in μA
0.1M	1.06	-1.8 V	11.655
0.1M	1.06	-1.8 V	11.535
0.5M	0.1	-1.85V	0.41
0.5M	0.1	-1.85V	0.53
0.5M	0.2	-1.85V	0.653
0.5M	0.2	-1.85V	0.93
0.5M	0.2	-1.85V	1.095

It was also seen that thorium ions increased the hydrogen overvoltage specially at high concentrations of lithium sulphate. For example, in a solution containing 0.5M lithium sulphate, current at -2.1 volts *vs.* S. C. E. was 4.3 μA (this is the region of liberation of hydrogen). On the other hand current, at the same voltage



1/15 Sodium Succinate in mls.
Fig. 1 - Sp. cond. and pH versus amount of Sod. Succ.



3 M/120 Sodium Succinate in mls.
Fig. 2 - Sp. cond. and pH versus amount of Sod. Succ.

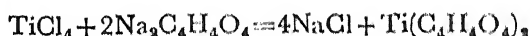
EXPERIMENTAL

A stock solution of titanous chloride is obtained by dissolving in cold concentrated hydrochloric acid. The titanium content, in such solution was found to be 11.834 gms/lit. The stock solution was then diluted to the desired concentrations. When employing dilute solutions care was always taken to employ fresh solutions as titanous chloride is greatly susceptible to hydrolysis.

The methods for the potentiometric and conductometric titrations were the same as described in our previous publications (1 - 4), 2.00 mls of M/4.048 titanous chloride were titrated against different amounts of M/5 sodium succinate solution. The total volume was kept 28.00 mls and the electrometric measurements were made at $32^{\circ} \pm 0.1^{\circ}\text{C}$. Our results with four different concentrations of the interacting solutions are represented in Figs. (1 to 4).

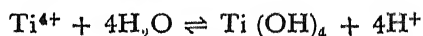
DISCUSSION

The interaction between a solution of titanous chloride and that of sodium succinate may be represented by the simple stoichiometric equation :



With the addition of larger and larger quantities of sodium succinate solution to a fixed amount of titanous chloride, the less conducting Ti^{4+} ions will be progressively replaced by the more conducting Na^+ ions. A gradual increase in the electrical conductance is, therefore, likely to be observed, till the above reaction is complete, and all the titanous ions are used up, after which the further addition of sodium succinate should bring about a steep rise in electrical conductance. An inspection of Figs. 1 to 4 shows that initially there is slight increase in electrical conductance followed by a drop proceeding up to a minimum after which there is a gradual increase.

The low pH (1.65 - 2.20) of titanous chloride solutions indicate that the solutions are fairly acidic due to the presence of free hydrochloric acid and due to the hydrolysis of the salt in a manner similar to zirconium and thorium salt solutions already investigated i.e. as follows :



The solutions of sodium succinate being alkaline due to the hydrolysis of the salt the slow initial rise in pH is evidently due to the removal of the hydrogen ions either (a) by the formation of water or (b) less ionised succinic acid



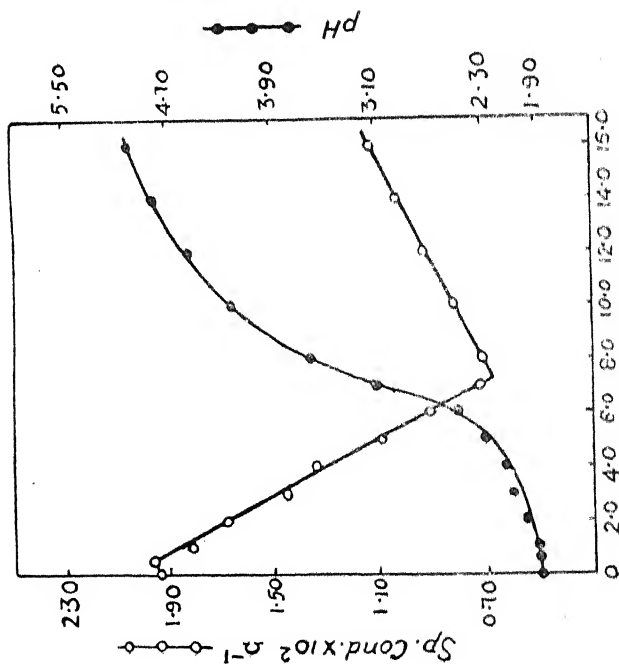


Fig. 3 - Sp. cond. and pH versus amount of Sod. Succ. N/10 Sodium Succinate in mls.

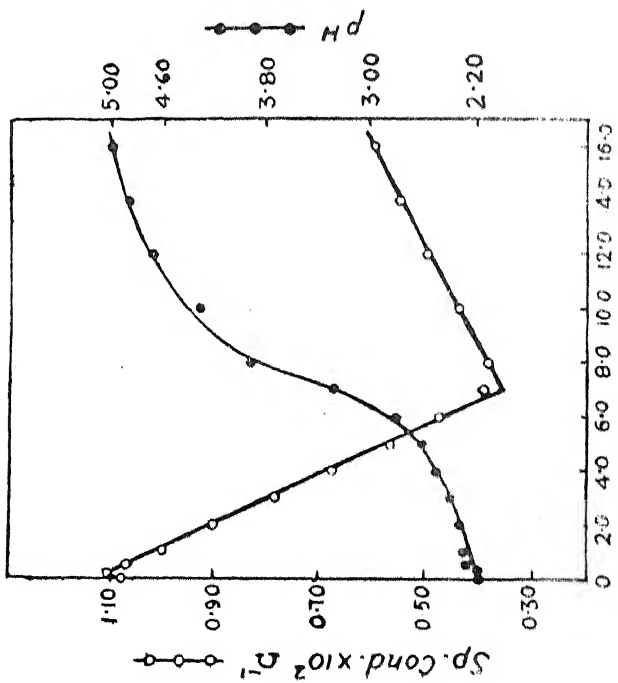


Fig. 4 - Sp. cond and pH versus amount of Sod. Succ. N/20 Sodium Succinate in mls

This scheme of interaction suggests a fall in electrical conductance due to the removal of highly conducting hydrogen ions. A rise in conductance is, however, perceivable in the early stages. This is explained on the basis that along with the removal of the hydrogen ions, Ti^{4+} ions are replaced by the more conducting Na^+ ions and consequently the latter effect predominating the former, a rise in conductivity is observed instead of a decrease.

When more of the alkaline succinate is added the decrease in the hydrogen ion concentration becomes more rapid and the conductance falls off rapidly, until a break in the conductance graph occurs, after which the conductance curve again rises, due to the presence of the excess of sodium succinate. An inflexion point in the pH curve corresponding to the break in the conductance curve is similarly noticed in Figs. 1 to 4.

It is interesting to note that the break in the conductance graph and the inflexion in the pH curve occur when the metal, succinate ratio is 1 : 3, *i.e.* the amount of sodium succinate used is much more than what is required in the formation of the metal di-succinate $\text{Ti}(\text{C}_4\text{H}_4\text{O}_4)_2$. This is highly probable as the metal salt solution being fairly acidic, part of the succinate is employed in reacting with the free hydrochloric acid and a part in the formation of the disuccinate. In order to ascertain how much succinate, out of the total added, was used to form the metal succinate, the total titanium and the chloride in the metal chloride solution was estimated. The free chloride due to HCl present was then calculated out. From this data the amount of sodium succinate used by the free hydrochloric acid was known. The rest of the sodium succinate combining with the metal is then known. At all the four concentrations of the interacting solutions investigated, it was found that the metal succinate (combined) ratio is 1 : 2, suggesting clearly the formation of the metal disuccinate *i.e.* 1.00 part of sodium succinate is free to react with hydrochloric acid. A typical set, of estimations and calculations, is presented here:

- (a) Total titanium = 11.834 gms/lit.
- (b) Total chloride = 45.630 gms/lit.
- (c) Chloride combined with titanium = 35.030 gms/lit.
- (d) Chloride free = 10.600 gms/lit.
- (e) Amount of sodium succinate used in reacting with free chloride (200 mls of TiCl_4 solution containing 11.834 gms of Ti/lit. with M/5 sodium succinate). = 1.494 mls.
- (f) Total sodium succinate (for 2.00 mls. of same TiCl_4 solutions). = 7.00 mls.
- (g) Amount of sodium succinate combined with the metal on the basis of the above = 5.50 mls.
- (h) Ratio of Ti : succinate (combined) = 1 : 2

It is evident that the interaction between sodium succinate and the metal chloride solution follows stoichiometric relation and the precipitate obtained as a result of the interaction between the two solutions is chiefly the metal di-succinate $Ti(C_4H_4O_4)_2$.

ACKNOWLEDGEMENT

Thanks of the authors are due to Prof. S. Ghosh, D.Sc., F.R.I.C., F.N.I. for kind interest during the progress of this work and to the Scientific Research Committee, Uttar Pradesh, for the award of a research scholarship to one of them (Y. D. U.)

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CHEMICAL EXAMINATION OF ANGELICA GLAUCA FRUIT

By

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[Received on 9th November, 1960]

Angelica glauca Edgq. (Fam. Umbelleferae) is known as Chora, locally. It is a glabrous herb and is distributed through out the Western Himalayas at 8000-10,000 ft. Medicinally it is used in the obstinate constipation, bilious complaints, and considered to be cordio active and stimulant. It is also used in flatulence and dyspepsia. No chemical investigation of the fruit of the plant appears to have been done. A lactonic constituent (m. p. 101-102°C) has been isolated from the petroleum ether extract of the fruit.

The fruits were powdered and extracted with petroleum ether (40-60) in soxhlet for 72 hours. On standing a crystalline substance separated out. The solvent was decanted off and concentrated when more of the same compound was obtained, the yield was nearly 0.6 per cent. The above exhausted drug was further extracted with ether, chloroform, methanol and ethanol. After partial removal of the solvents only viscous liquids were obtained which did not yield any crystalline substance. These were also chromatographed over a column of alumina using various solvents for elution but nothing crystalline could be obtained.

The solid obtained was crystallised number of times from methanol when it came down as flakes m. p. 101-102°C. It was slightly yellow in colour and was fairly soluble in organic solvents. It was optically inactive, neutral to litmus and did not give carbon dioxide with sodium bicarbonate or carbonate solutions. It decolourised acid potassium permanganate solution and its solution in carbon tetrachloride absorbed bromine but the bromo derivative could not be crystallised. The substance dissolved in alcoholic potash and on acidification was regenerated thus showing presence of lactonic system in the compound. It did not give a semi-carbazone or 2:4 dinitrophenyl hydrozone. It gave acetate (needles m. p. 153-55°C) and benzoate m. p. 199-120°C.

Found C, 66.24; H, 14.16; Mol. Wt. 246 (Rast); $C_{14}H_{26}O_8$ requires C, 66.6; H, 14.2.

I. R. spectrum in Nujol has shown the absorption peaks at 1724 cm^{-1} (S) for R_{COO-} ; 1581 cm^{-1} (S) for conjugated with aromatic ring; 1346 cm^{-1} ; 1155 cm^{-1} (S) for $-C-OH$; 1289 cm^{-1} for $-CO-O-$.

U. V. absorption in alcoholic solution has shown the maxima at 306 and 250 $m\mu$.

Further work on the compound and other extracts is in progress.

THE ROTATORY POWER OF STRYCHNINE-*p*-NITRO BENZOATE IN CHLOROFORM

By

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[Received on 26th October, 1960]

ABSTRACT

Strychnine-*p*-nitro benzoate is soluble in benzene and pyridine but whereas in pyridine it shows optical rotation, in chloroform it shows no rotation. A study of the optical rotation of this compound in a mixture of pyridine and chloroform reveals that its zero rotation in chloroform is not due to racemization but is a purely solvent effect.

INTRODUCTION

In an earlier communication¹ it was pointed out that strychnine-*p*-nitrobenzoate though soluble in chloroform like strychnine-*o*-nitrobenzoate and strychnine-*m*-nitrobenzoate shows zero rotation in this solvent. In the present investigation a determination of rotatory power in a mixture of pyridine and chloroform has been carried out with a view to throw light on the anomalous behaviour of strychnine-*p*-nitrobenzoate in chloroform.

EXPERIMENTAL

Strychnine-*p*-nitrobenzoate was prepared according to the method described earlier¹. In Table 1 are given the values of specific rotation for Hg 5461 in a mixture of pyridine and chloroform in different proportions. The concentrations used for each determination were approximately the same and rotatory power measurements were carried out in a 2 dcm. tube within a narrow range of temperature.

TABLE 1

Comparison of rotatory power of strychnine-*p*-nitro-benzoate in mixtures of chloroform and pyridine

S. N.	Conc. in g./100 ml	Temp. °C	Solvent		Sp. rotation for Hg 5461
			% Pyridine	% Chloroform	
1.	1.0000	15.5	100	0	-97.00°
2.	1.0024	11.5	90	10	94.27
3.	1.0044	12.0	80	20	85.62
4.	1.0016	12.5	70	30	79.87
5.	1.0008	12.5	60	40	78.93
6.	1.0020	13.0	50	50	72.85
7.	1.0044	13.0	40	60	69.19
8.	1.0012	13.0	30	70	66.41
9.	0.9972	12.5	20	80	58.66
10.	1.0032	12.5	10	90	46.35
11.	1.0012	19.5	5	95	38.95
12.	1.0008	20.0	1	99	30.47
13.	1.0016	19.5	0.4	99.6	23.96
14.	1.0000	19.5	0	100	0.00

When strychnine-*p*-nitro-benzoate was dissolved in chloroform, it showed zero rotation. Chloroform was removed and the solute recovered. This was dissolved in pyridine and was found to show a sp. rotation for Hg 5461 equal to -97.00°.

DISCUSSION

The zero rotation of strychnine-*p*-nitro-benzoate in chloroform is not due to racemization as when the solvent chloroform is removed and the recovered solute dissolved in pyridine, it gives the same rotation as that obtained in the solution of strychnine-*p*-nitro-benzoate in pyridine. It has also been noticed earlier¹ that in the case of strychnine-*o*-nitro-benzoate the magnitude of specific rotation for Hg 5461 in pyridine is 85.00° and in chloroform it is only 26.50°. Likewise, in the case of strychnine-*m*-nitro-benzoate the corresponding values are 94.04° and 5.51°. It is, however, only in the case of strychnine-*p*-nitro-benzoate that the rotation in chloroform falls to a zero value.

From Table 1 it is seen that the magnitude of rotation of strychnine-*p*-nitro-benzoate in pyridine falls off as chloroform is added to it. This indicates that the solvent chloroform and pyridine are acting independently of each other in a mixture of the two. The anomalous behaviour of strychnine-*p*-nitro-benzoate in chloroform is probably purely due to solvent.

It is worth pointing out here that in a consideration of the influence of the solvent on rotatory power two types of cases may arise giving anomalous behaviour. Firstly, the solvent may form a chemical compound with the active solute² as in the case of octyl iodoacetate dissolved in pyridine³ or L-menthyl hydrogen naphthalate dissolved in basic solvents⁴. Secondly, when the solvent does not enter into chemical combination with the solute. A case of this type was observed by Pribram⁵ in 5% solution of *dextro* tartaric acid in different solvents. He observed that whereas *dextro* tartaric acid gives a positive value of $[\alpha]_D^{20}$ in water (+14.40°) and ethanol (+3.79°), in a mixture of ethanol and benzene (1 : 1) it gives a value of -4.11°, in ethanol and toluene (1 : 1) -6.19° and in ethanol and chlorobenzene (1 : 1) -8.09°. From this study it is obvious that solvent can not only influence the magnitude of rotation but it can also effect the direction of rotation. Even in the example studied by Pribram it is obviously possible to obtain zero rotation in a suitable mixture of solvents. In the case studied by us it is clear that the effect of chloroform is not due to chemical combination with the optically active solute. This case is in some ways similar to that studied by Pribram.

Further investigation of this interesting case is being carried out.

ACKNOWLEDGEMENT

We wish to make a grateful acknowledgement to the authorities of Th. D. S. B. Government College, Naini Tal, for the provision of research facilities and to Scientific Research Committee, U. P. for the grant of an assistantship to one of us (B. C. P.).

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SYNTHESIS AND REACTIONS OF *α*-BROMO *α*-*iso*-NITROSO-*p*-METHYL ACETOPHENONE, *α*-BROMO-*α*-*iso*-NITROSO METHYL-*β*-NAPHTHYL KETONE AND *α*-BROMO-*α*-NITROSO METHYL ETHYL KETONE

By

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ABSTRACT

Synthesis, characterisation and reactions of *α*-bromo-*α*-*iso*-nitroso-*p*-methyl acetophenone, *α*-bromo-*α*-*iso*-nitroso-methyl-*β*-naphthyl ketone and *α*-bromo-*α*-nitroso methyl ethyl ketone have been described.

INTRODUCTION

In earlier communications^{1,2} one of us has described the preparation and properties of some *α*-bromo-*α*-*iso*-nitroso ketones. The present work is an extension of the earlier work. In this paper is described the synthesis and reactions of *α*-bromo-*α*-*iso*-nitroso-*p*-methyl acetophenone, *α*-bromo-*α*-*iso*-nitroso-methyl-*β*-naphthyl ketone and *α*-bromo-*α*-nitroso methyl ethyl ketone.

EXPERIMENTAL

Synthesis of α-bromo-α-iso-nitroso-p-methyl acetophenone :

Method I : The sodium salt of *iso*-nitroso-*p*-methyl ketone was prepared and its direct bromination tried as in the case of acetophenone described earlier.² The solid product obtained was crystallised from benzene. Its m. p. was 178° and was found to be solely *p*-methyl benzoic acid.

Method II : In this method the bromination of copper complex was tried. Its copper complex was obtained in a manner similar to those described earlier.¹ The copper complex had m. p. 130°d. (Found: Cu 16.9 % ; C₁₈H₁₆O₄N₂Cu requires Cu = 16.3 %) The copper complex (20g) was suspended in dry ether (50ml) and benzene (10ml), the solution was well cooled and bromine (16.6g) was added to it. The whole was kept over night, washed twice with water and dried over anhydrous magnesium sulphate. On evaporation it gave a solid mass which was crystallised from carbon tetrachloride Yield 4.2 g : m. p. 132°; Found N = 6.03 % , Br = 33.23 % , C₉H₈O₂NBr requires N = 5.78 % , Br = 33.06%.

Method III : In this method direct nitrosation of *p*-methyl phenacyl bromide was tried in a manner similar to that described for *α*-bromo-*α*-*iso*-nitroso acetophenone described earlier.¹ Starting from 6.4 g *p*-methyl phenacyl bromide, 50 ml ether and 2.7 g isopropyl nitrite a product with m. p. 130° was obtained in 3.86 g yield. It was found to contain chlorine and analysis showed it to be *α*-chloro-*α*-*iso*-nitroso-*p*-methyl acetophenone. (Found : C = 53.9 % , H = 4.05 % , N = 6.86 % , Cl = 17.1 % ; C₉H₈O₂NCl requires C = 54.6 % , H = 4.05 % , N = 6.5 % , Cl = 17.9 %).

The attempt for direct nitrosation was repeated by modifying the method. *p*-Methyl phenacyl bromide (3.2 g) and ether (50 ml) saturated with hydrogen chloride gas were taken and isopropyl nitrite (1.4 g) was added drop by drop with constant stirring. The reaction time was limited to two and a half hours. The organic layer was then separated, washed twice with water, dried over anhydrous sodium sulphate and ether removed. The solid obtained was dried in vacuum and recrystallised from carbon tetrachloride. Yield 2.0 g, m. p. 132°. Found : Br

= 33.89 %, $C_9H_8O_2NBr$ requires Br = 33.06 %. It was found to be the desired bromo compound.

a-bromo-*a*-iso-nitroso-*p*-methyl acetophenone is a colourless crystalline solid. It is soluble in benzene, ether, alcohol, chloroform and acetone. It is insoluble in water.

It does not give any colour with alcoholic ferric chloride solution immediately but on standing develops a violet colour. It does not liberate iodine on being warmed with acidified potassium iodide solution. It reduces Fehling's solution and gives a wine red colour with pyridine. It is a lachrymator in solution.

Synthesis of a-bromo-a-iso-nitroso methyl-β-naphthyl ketone :

Method I : Bromination of copper complex was tried in a manner similar to that described in Method II for the preparation of *a*-bromo-*a*-iso-nitroso-*p*-methyl acetophenone. The amounts used were copper chelate of isonitroso methyl-β-naphthyl ketone (4.6 g), ether (30 ml), benzene (15 ml) and bromine (3.22 g). The product was crystallised from a mixture of carbon tetrachloride (1 part) and benzene (2 parts). Yield 1.9 g, m. p. 152°; Found : Br = 29.1%, $C_{12}H_8O_2NBr$ requires Br = 28.77 %.

Method II : In this method the nitrosation of bromo methyl-β-naphthyl ketone in presence of hydrogen chloride was tried.

Bromo-methyl-β-naphthyl ketone was obtained by direct bromination of methyl-β-naphthyl ketone in acetic acid medium. The product obtained had m. p. 82°. Found : Br = 32.3%, $C_{12}H_8OBr$ requires Br = 32.1%.

The nitrosation of bromo methyl-β-naphthyl ketone was carried out according to the modification described in Method III for *a*-bromo-*a*-iso-nitroso-*p*-methyl acetophenone. The quantities used were bromo methyl-β-naphthyl ketone 2.5 g, ether saturated with hydrogen chloride gas 30 ml and isopropyl nitrite 1 g. The crude product obtained was crystallised from a mixture of carbon tetrachloride and benzene (1 : 3). Yield 2.8 g, m. p. 152°. Found : N = 4.70 %, Br = 29.00 %; $C_{12}H_8O_2NBr$ requires N = 5.03 %, Br = 28.77 %.

It is a yellowish white crystalline solid. It is soluble in alcohol, benzene and ether, sparingly so in petroleum ether and carbon tetrachloride, and insoluble in water.

It does not give any immediate colour with alcoholic ferric chloride solution but develops a violet colour on long standing. Like *a*-bromo-*a*-iso-nitroso-*p*-methyl acetophenone it reduces Fehling's solution, does not liberate iodine from acidified potassium iodide solution, and gives a wine red colour with pyridine.

Synthesis of a-bromo-a-nitroso methyl ethyl ketone :

Direct bromination of the sodium salt of *iso*-nitroso methyl ethyl ketone gave a thick syrupy liquid which was highly lachrymatory but which showed the presence of both nitrogen and bromine (cf. Method I in the case of synthesis of *a*-bromo-*a*-iso-nitroso-*p*-methyl acetophenone). Bromination in pyridine yielded only acetic acid (cf. synthesis of *a*-bromo-*a*-isonitroso acetophenone described earlier²). Bromination of copper complex in the manner described in Method II for the preparation of *a*-bromo-*a*-iso-nitroso-*p*-methyl acetophenone yielded a gummy product which was highly lachrymatory. From this a small amount of crystalline

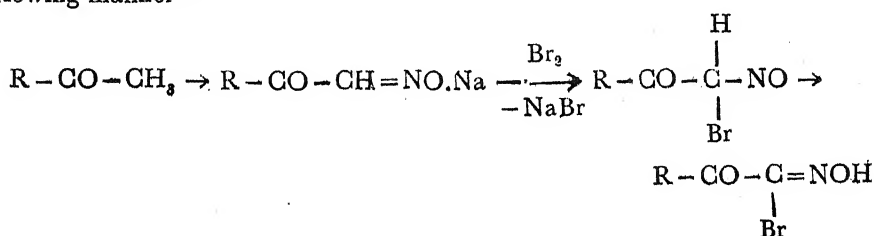
product was extracted with petroleum ether which showed a m. p. of approximately 81°. Bromination in ether in presence of marble was then tried.

Isonitroso methyl ethyl ketone (5 g) and dried ether (25 ml) were taken in a reaction flask along with a piece of marble. The mixture was cooled in ice and bromine (1.3 ml) was added drop by drop with constant stirring for two and a half hours. It was allowed to stand in the refrigerator for 36 hours to complete the reaction. The ether was removed and the residue crystallised from carbon tetrachloride. Yield 4.6 g, m. p. 83-84°. Found: C = 27.75 %, H = 3.51 %, N = 7.7 %, Br = 44.98 %; $C_4H_8O_2NBr$ requires C = 26.6 %, H = 3.3 %, N = 7.7 %, Br = 44.4 %.

It is a colourless crystalline solid. It is soluble in benzene, ether, alcohol and acetone, and sparingly soluble in water and carbon tetrachloride. It reduces Fehling's solution and gives a yellow colour with pyridine. It liberates iodine when warmed with acidified potassium iodide solution. It does not immediately give any colour with alcoholic ferric chloride solution but on standing develops a yellow colour.

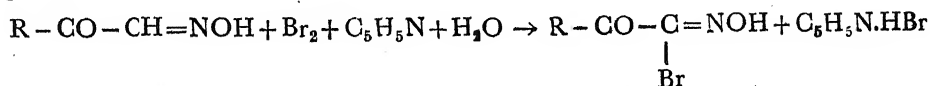
DISCUSSION

Bromination of sodium salt of *iso*-nitroso ketones should normally proceed in the following manner—



Here it is found that in the case of sodium salt of *iso*-nitroso-*p*-methyl ketone only *p*-methyl benzoic acid was obtained and in the case of *iso*-nitroso methyl ethyl ketone a syrupy product was obtained which, however, was found to show the presence of both nitrogen and bromine in it. In the cases studied earlier, namely, the sodium salts of *iso*-nitroso acetophenone, isonitroso (*p*-methyl, *p*-methoxy, *p*-chloro and *p*-bromo) acetophenones it was found that direct bromination yielded only the corresponding acids.² In all probability the normal course of the reaction is changed because of the presence of alkali, NaOBr and bromine which may oxidise the bromo compound to the corresponding acid. Where only the corresponding acid is obtained this oxidation reaction goes to completion but where a syrupy product is obtained indicating formation of mixtures, the oxidation evidently is not complete. This explanation is supported by the fact that oxidative fission of some bromo-*iso*-nitroso ketones yields corresponding acids^{1,2}. This clearly indicates that bromination of sodium salt of isonitroso ketones is not a suitable method for preparing bromo-*iso*-nitroso ketones.

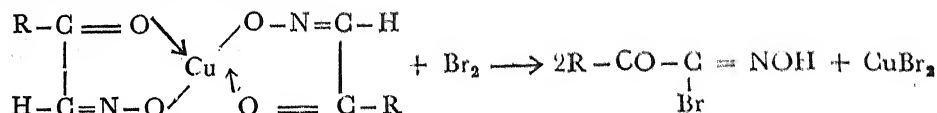
Direct bromination of free *iso*-nitroso ketones in pyridine can be expected to proceed in the manner indicated below—



In the case of *iso*-nitroso methyl ethyl ketone the reaction, however, yielded only acetic acid. This was perhaps due to the oxidation of free *iso*-nitroso ketone by bromine. Similar unsatisfactory results were obtained when the medium used was

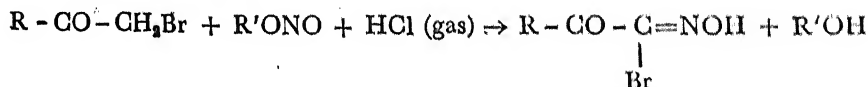
either when the reaction was very slow. However, when bromination in ether medium in presence of marble was tried in the case of *iso*-nitroso methyl ethyl ketone the bromination was found to proceed smoothly. The role of ether and marble is not clear but there is little doubt that they prevent the oxidation of free *iso*-nitroso ketones by bromine.

Bromination of copper complex of *iso*-nitroso ketones generally proceeds smoothly in the following manner—



where R is H, CH₃-, C₂H₅-, C₆H₅, CH₃-C₆H₄-, CH₃O-C₆H₄-, Cl-C₆H₄-, C₁₀H₇-(See ref. 1, 2 and this paper). This bromination is known to be slow in the case of *iso*-nitroso ketones and hence in some cases such as in the case of copper complex of *iso*-nitroso methyl ethyl ketones described in this paper the product is a gummy mass indicating the presence of more than one substance presumably due to the oxidising action of bromine.

The other method for obtaining α -bromo- α -isonitroso ketones is to carry out nitrosation of α -bromo ketones. This is done by the help of alkyl nitrite in ether in presence of hydrogen chloride gas when the reaction normally proceeds in the following manner—



It was noticed by the authors that if the time of reaction is prolonged as in the case of nitrosation of *p*-methyl phenacyl bromide, α -chloro- α -*iso*-nitroso-*p*-methyl acetophenone is obtained instead of α -bromo- α -*iso*-nitroso-*p*-methyl acetophenone (see also ref. 2). As explained earlier in the case of phenacyl bromides the replacement of bromine by chlorine in this case may be caused by the presence of excess of hydrogen chloride or prolonged contact with it or heating done to remove solvent at a later stage. To obviate this undesirable course of action it is best to reduce the time of reaction when only the α -bromo- α -*iso*-nitroso ketone would be produced.

When we compare the properties of the α -bromo- α -*iso*-nitroso ketones described in this paper we notice that whereas α -bromo- α -*iso*-nitroso-*p*-methyl acetophenone and α -bromo- α -*iso*-nitroso-methyl- β -naphthyl ketone do not liberate iodine from acidified potassium iodide solution, the α -bromo- α -nitroso methyl ethyl ketone does so. An explanation of this difference in behaviour of the bromine atom is to be found by considering its nature in these two types of compounds. Where the iodine is not liberated the compound is capable of being considered as an acid halide of hydroxamic acid of the type R-CO-CX=NOH whereas in the case when iodine is liberated the compound is incapable of being considered as an acid halide of hydroxamic acid and remains a true α -bromo ketone. The acid halides can not be expected to liberate iodine from acidified potassium iodide whereas the true α -bromo ketones can do so easily.

ACKNOWLEDGEMENTS

The authors are grateful to the authorities of Th. D. S. B. Government College, Naini Tal, for providing research facilities.

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AN EXACT SOLUTION IN FINITE STRAIN

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1. INTRODUCTION

The problem of an incompressible spherical shell under radial body force with special reference to a self-gravitating shell has been solved by B. R. Seth (1) on the basis of linear stress-strain relations. It is proposed to generalise Seth's result and obtain an exact solution for this problem in terms of the strain energy function W . Some numerical values have been obtained for a neo-hookean solid and compared with those obtained in (1).

Notation and Formulae

Following the notation of Green and Zerna (2), the summary of the formulae required are given below.

Let x_i be the initial, y_i the final and θ_i the curvilinear coordinates of the strained body.

The covariant and contravariant base vectors g_i and g^i of the curvilinear system θ_i at a point P_0 of an unstrained body are given by

$$\begin{aligned} g_i &= r_{,i} ; g = g^{ij} g_j ; g = |g_{ij}| \\ g_{ij} &= g_i \cdot g_j ; g^{ij} = g^i \cdot g^j ; g^{ij} g_{jk} = \delta_k^i \end{aligned} \quad (1.1)$$

where $r(\theta_1, \theta_2, \theta_3)$ is the position vector of P_0 and a comma denotes partial differentiation.

In the strained state let the point P_0 move to the point P at time t . If the displacement vector $P_0 P$ is $d(\theta_1, \theta_2, \theta_3)$, the covariant and contravariant base vectors at P of the curvilinear system θ_i are given by

$$\begin{aligned} G_i &= r_{,i} + d_{,i} ; G^i = G^{ij} G_j ; G = |G_{ij}| \\ G_{ij} &= G_i \cdot G_j ; G^{ij} = G^i \cdot G^j ; G^{ij} G_{jk} = \delta_k^i \end{aligned} \quad (1.2)$$

When the unstrained body is homogenous and isotropic, the strain-energy function W , measured for unit volume of the unstrained body, is a function of the strain invariants, so that

$$W = W(I, II, III) \quad (1.3)$$

where $I = g^{ij} G_{ij}$; $II = g_{ij} G^{ij}$; $III = G/g$.

The contravariant stress-tensor measured per unit area of the strained body referred to θ_i coordinates is expressed in the form

$$T^{ij} = g^{ij} \phi + B^{ij} \psi + G^{ij} p \quad (1.4)$$

$$\text{where } \phi = 2 \frac{\partial W}{\partial I} / III^{1/2}; \psi = 2 \frac{\partial W}{\partial II} / III^{1/2}; p = 2 III^{1/2} \frac{\partial W}{\partial III}$$

$$B^{ij} = g^{ir} g^{js} G_{rs} = \epsilon^{irm} \epsilon^{ism} G_{mn} / g \quad (1.5)$$

and, as usual ϵ is +1 or -1 according as r, s, t is an even or odd permutation of 1, 2, 3 and equal to zero otherwise. The physical components of stress σ_{ij} are given by

$$\sigma_{ij} = (G_{jj} / G^{ii})^{1/2} T^{ij} \quad (1.6)$$

When the material is incompressible, the equation $III = 1$ holds at all points of the body, and the strain-energy function W is a function of I and II only. In this case p is a scalar invariant function of the coordinates θ_i for each value of the time t .

The equation of equilibrium can be expressed in the form

$$T^{ij}_{,i} + \rho F^j = 0 \quad (1.7)$$

where the comma denotes covariant differentiation with respect to the strained body and F^j are the contravariant components of the body force vector referred to the covariant base vectors G_i .

2. SPHERICAL SHELL UNDER RADIAL BODY FORCE WITH SPECIAL REFERENCE TO A SELF-GRAVITATING SHELL

Specification of curvilinear system of coordinates

Let the curvilinear system of coordinates θ_i in the strained body be identified with a system of spherical polar coordinates (R, θ, ϕ) with origin at the centre of the shell, so that

$$\theta_1 = R, \theta_2 = \theta, \theta_3 = \phi \quad (2.1)$$

$$y_1 = R \sin \theta \cos \phi, y_2 = R \sin \theta \sin \phi, y_3 = R \cos \theta \quad (2.2)$$

Deformation of the spherical shell and metric tensors

Let the inner and outer radii of the shell in the deformed state be R_1 and R_2 respectively. Since the shell is under radial body force, it is strained symmetrically. Therefore, we can assume that the point (R, θ, ϕ) in the strained state was originally at the point (r, θ, ϕ) in the unstrained state so that

$$r = f(R) \quad (2.3)$$

If x_i - axes coincide with y_i - axes, we have

$$x_1 = f \sin \theta \cos \phi, x_2 = f \sin \theta \sin \phi, x_3 = f \cos \theta \quad (2.4)$$

where $f = f(R)$.

The metric tensors for the strained and unstrained bodies are

$$G^{ij} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1/R^2 & 0 \\ 0 & 0 & 1/R^2 \sin^2 \theta \end{bmatrix}, \quad G_{ij} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & R^2 & 0 \\ 0 & 0 & R^2 \sin^2 \theta \end{bmatrix}, \quad G = R^2 \sin^2 \theta \quad (2.5)$$

$$g^{ij} = \begin{bmatrix} 1/f_R^2 & 0 & 0 \\ 0 & 1/f^2 & 0 \\ 0 & 0 & 1/f^2 \sin^2 \theta \end{bmatrix}, \quad g_{ij} = \begin{bmatrix} f_R^2 & 0 & 0 \\ 0 & f^2 & 0 \\ 0 & 0 & f^2 \sin^2 \theta \end{bmatrix}, \quad g = f^4 \int_R^2 \sin^2 \theta \quad (2.6)$$

where $f_R = \frac{df}{dR}$.

Condition of incompressibility and evaluation of constants.

The condition of incompressibility $III=1$ gives

$$f^4 f_R^2 = R^4 \quad (2.7)$$

so that $r^3 = f^3 = R^3 - A$

where A is a constant to be determined.

If the inner and outer radii of the shell in the unstrained state are denoted by r_1, r_2 respectively, the equation 2.8 gives

$$A = R_1^3 - r_1^3 = R_2^3 - r_2^3 = R^3 - r^3 \quad (2.9)$$

$$f^3 = R^3 + r_1^3 - R_1^3 \quad (2.10)$$

From the equations (2.6) and (2.7) we obtain

$$g^{ij} = \begin{bmatrix} f^4/R^4 & 0 & 0 \\ 0 & 1/f^2 & 0 \\ 0 & 0 & 1/f^2 \sin^2 \theta \end{bmatrix}, \quad g_{ij} = \begin{bmatrix} R^4/f^4 & 0 & 0 \\ 0 & f^2 & 0 \\ 0 & 0 & f^2 \sin^2 \theta \end{bmatrix}, \quad g = R^4 \sin^2 \theta \quad (2.11)$$

Substituting (2.5) and (2.11) in (1.4) and (1.5) we get

$$B^{ij} = \begin{bmatrix} 2f^3/R^3 & 0 & 0 \\ 0 & f^2/R^4 + R^2/f^4 & 0 \\ 0 & 0 & (f^6 + R^6)/f^4 R^4 \sin^2 \theta \end{bmatrix} \quad (2.12)$$

$$\begin{aligned} T^{11} &= f^4 \phi/R^4 + 2f^2 \psi/R^3 + p \\ T^{22} &= T^{33} \sin^2 \theta = \phi/f^2 + (f^2/R^4 + R^2/f^4) \psi + p/R^2 \\ T^{23} &= T^{31} = T^{12} = 0. \end{aligned} \quad (2.13)$$

Equations of equilibrium

The three equations of equilibrium (1.7) which must be satisfied, reduce with the help of (2.5) and (2.13) to

$$\frac{dT^{11}}{dR} + \frac{2T^{11} - (R^2 T^{22} + R^2 \sin^2 \theta T^{33})}{R} + \rho F^1 = 0 \quad (2.14)$$

$$R \frac{\partial T^{22}}{\partial \theta} + \rho F^2 = 0; \quad R \sin \theta \frac{\partial T^{33}}{\partial \phi} + \rho F^3 = 0 \quad (2.15)$$

To be able to proceed further, we should know R^i . If we take the case of a self-gravitating shell, we have

$$F^1 = -4\pi (R^3 - R_1^3)/3R^2, F^2 = 0 \text{ and } F^3 = 0 \quad (1.16)$$

Substituting (2.13) and (2.16) in (2.14) and (2.15) we get

$$T^{11} = f^R \left[(2R^6 - f^6) (\psi/f^2 + \phi/R^2) R^3 f^2 + 4\pi\rho (R^3 - R_1^3)/3R^2 \right] \quad (2.15)$$

$$dR = \text{constant} \quad (2.17)$$

$$\frac{\partial p}{\partial \theta} = 0 \text{ and } \frac{\partial p}{\partial \phi} = 0 \quad (2.18)$$

The equations (2.18) show that p is a function of R only.

From (1.3), (2.5) and (2.11), we get

$$I = f^4/R^4 + 2R^2/f^2 \quad (2.19)$$

$$II = 2f^2/R^2 + R^4/f^2 \quad (2.20)$$

$$\frac{dI}{dR} = -4(R^3 - f^3)^2 (R^3 + f^3)/R^5 f^5 \quad (2.21)$$

$$\frac{dII}{dR} = -4(R^3 - f^3)^2 (R^3 + f^3)/R^3 f^7 \quad (2.22)$$

Therefore

$$\frac{dW}{dR} = \frac{\partial W}{\partial I} \frac{\partial I}{\partial R} + \frac{\partial W}{\partial II} \frac{dII}{dR} = \left[\frac{2(R^6 - f^6) (\psi/f^2 + \phi/R^2)/R^3 f^2}{(f^3 - R^3)/f^3} \right] \quad (2.23)$$

substituting (2.23) in (2.17), we get

$$T^{11} = f^R \left[\frac{dW}{dR} \frac{f^3}{f^3 - R^3} + 4\pi\rho (R^3 - R_1^3)/3R^2 \right] \quad (2.24)$$

$dR = \text{Constant}$

Boundary conditions and the physical components of stress

The boundary conditions require that

$$(i) T^{11} = 0 \text{ on } R = R_1 \quad (2.25)$$

This is satisfied if

$$T^{11} = \int_{R_1}^R \left[\frac{dW}{dR} \frac{f^3}{f^3 - R^3} + 4\pi\rho (R^3 - R_1^3)/3R^2 \right] dR \quad (2.26)$$

substituting T^{11} from (2.13) in this equation, we get the value of p as

$$p = -f^4 \phi/R^4 - 2f^2 \psi/R^2 + \int_{R_1}^R \left[\frac{dW}{dR} \frac{f^3}{f^3 - R^3} + 4\pi\rho (R^3 - R_1^3)/3R^2 \right] dR \quad (2.27)$$

$$(ii) T^{11} = 0 \text{ on } R = R_2 \quad (2.28)$$

This is satisfied if

$$\int_{R_1}^R \left[\frac{dW}{dR} \frac{f^3}{f^3 - R^3} + 4\pi \rho (R^3 - R_1^3)/3R^2 \right] dR = 0 \quad (2.29)$$

The equation (2.9) and (2.29) determine the values of r_1, r_2 if R_1, R_2 and the form of the strain-energy function W are known and enables us to calculate the change in the thickness of the self-gravitating shell.

The non-vanishing physical components of stress are given by (1.6), (2.13) and (2.26) as

$$\sigma_{11} = \int_{R_1}^R \left[\frac{dW}{dR} \frac{f^3}{f^3 - R^3} + 4\pi \rho (R^3 - R_1^3)/3R^2 \right] dR \quad (2.30)$$

$$\sigma_{22} = \sigma_{33} = \sigma_{11} + \phi (R^2/f^2 - f^4/R^4) + \psi (R^4/f^4 - f^2/R^2) \quad (2.31)$$

For a neo-Hookean solid, the strain-energy function W is given by

$$W = c_1 (I - 3) \quad (2.32)$$

By substituting this value of W in (2.29), (2.30) and (2.31) and integrating, we get

$$c_1 \left[(r_2/R_2)^4 + 4(r_2/R_2) - (r_1/R_1)^4 - 4(r_1/R_1) \right] + \frac{2\pi\rho}{3} \left[R_2^2 - R_1^2 + 2R_1^3(1/R_2 - 1/R_1) \right] = 0 \quad (2.33)$$

$$\sigma_{11} = c_1 \left[(r/R)^4 + 4(r/R) - (r_1/R_1)^4 - 4(r_1/R_1) \right] + \frac{2\pi\rho}{3} \left[R^2 - R_1^2 + 2R_1^3(1/R - 1/R_1) \right] \quad (2.34)$$

$$\sigma_{22} = \sigma_{33} = \sigma_{11} + 2c_1 \left[(R/r)^2 - (r/R)^4 \right] \quad (2.35)$$

Taking $R_1/\sqrt{c_1/\rho} = 0.6$ and $R_2/\sqrt{c_1/\rho} = 0.9$ we get from (2.9) and (2.33) $r_1/\sqrt{c_1/\rho} = 0.65$ and $r_2/\sqrt{c_1/\rho} = 0.92$, giving the change in the thickness of the shell as $0.03\sqrt{c_1/\rho}$. The radial displacement $u_r = (r - R)$ and the distribution of stresses have been calculated and are given in the table below.

TABLE

$R/\sqrt{c_1/\rho}$	0.60	0.65	0.70	0.75	0.80	0.85	0.90
$u_r/\sqrt{c_1/\rho}$	0.045	0.039	0.034	0.030	0.026	0.023	0.021
σ_{11}/c_1	0.000	0.118	0.181	0.187	0.157	0.095	0.000
$\sigma_{22}/c_1 = \sigma_{33}/c_1$	0.937	0.862	0.772	0.672	0.558	0.430	0.288

The table shows that u_r and σ_{22} are maximum at the inner surface of the shell as in the previous result (1). The radial stress σ_{11} increases from zero at the inner surface of the shell and attains the maximum value at half-way through the material and gradually decreases to zero at the outer surface, whereas in Seth's result (1), it increases monotonically from zero at the inner surface of the shell and jumps suddenly to zero showing a discontinuity at the outer surface.

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FINITE BENDING OF PLATES. I

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1. INTRODUCTION

The theory of finite strain has been developed on the hypothesis that the second order terms in the components of strain may not be neglected (1, 2, 3). In the case of incompressible and isotropic materials number of problems have been solved completely (4, 5) without any restriction on the magnitude of the deformation or on the form of the strain energy function. However, in the case of compressible materials the solutions of the general equations in terms of the strain energy function are not always possible. In solving such problems number of writers suggested special assumptions regarding the strain energy function. These are generally based on apparent simplicity in some Mathematical frame work. B. R. Seth (1) adopted a linear stress-strain relation

$$t_{ij} = \lambda I \delta_{ij} + 2 \mu e_{ij} \quad (1.1)$$

in solving a variety of problems in finite strain. In two recent papers (6, 7) he considered approximate solutions which may be used to discuss the finite bending of circular plates into spherical shells. In this paper we obtain an exact solution for the above problem. It is shown that an exact solution can be obtained only when the ratio (the radius of the circular plate a /the radius of the spherical shell r) is so small that $\sin(a/r)$ can be replaced by (a/r) . The problem has been formulated by establishing one to one correspondence between the elements of the undeformed and deformed bodies, which gives an elegant and simple result directly. The results have been compared with those obtained by Seth (6, 7). The case of an incompressible plate, physically impossible in (6), has been discussed in detail in section 4.

It is proposed to extend the results to the cases of initially curved and anisotropic plates.

2. COMPONENTS OF STRAIN

Following the notation of Green and Zerna (5), let x_i be the initial and y_i the final and θ_i the curvilinear coordinates of the strained body, with g_{ij} and G_{ij} as metric tensors for the coordinate system θ_i in the unstrained and strained states of the body respectively. Then the state of strain is measured by the symmetric co-variant strain tensor ϵ_{ij} given by

$$2 \epsilon_{ij} = G_{ij} - g_{ij} \quad (2.1)$$

Introducing the displacement vector

$$V = V_i G^i = V^i G_i$$

where G^i and G_i are contravariant and covariant base vectors of the strained body, (2.1) reduces to

$$2 \varepsilon_{ij} = V_{i,j} + V_{j,i} - V_{,i}^r V_{r,j} \quad (2.2)$$

where comma denotes covariant differentiation with respect to the strained body.

The tensor components of strain can be replaced by physical components (8) if the former are orthogonal. The physical components denoted by e_{ij} are given by

$$e_{ij} = (G^{ii} G^{jj})^{1/2} \varepsilon_{ij} \quad (2.3)$$

Introducing the physical components of displacement u_i along θ_i coordinate curves in the strained body given by

$$u_i = V^i (G_{ii})^{1/2} \quad (2.4)$$

we can calculate the strain components for any convenient set of coordinates in the strained body.

If $\theta_1 = r$, $\theta_2 = \theta$ and $\theta_3 = \phi$ and $u_1 = u_r$, $u_2 = u_\theta$ and $u_3 = u_\phi$, we get the strain components in polar coordinates as

$$\begin{aligned} 2e_{rr} &= 2(u_r)_r - [(u_r)_r^2 + (u_\theta)_r^2 + (u_\phi)_r^2] \\ 2e_{\theta\theta} &= \frac{2}{r} [u_r + (u_\theta)_\theta] - \frac{1}{r^2} [A^2 + B^2 + (u_\phi)_\theta^2] \\ 2e_{\phi\phi} &= \frac{2}{r} [u_r + u_\theta \cot \theta + (u_\phi)_\phi / \sin \theta] - \frac{1}{r^2 \sin^2 \theta} [C^2 + D^2 + E^2] \\ 2e_{r\theta} &= \frac{1}{r} [r(u_\theta)_r - u_\theta + (u_r)_\theta] - \frac{1}{r} [A(u_r)_r + B(u_\theta)_r + (u_\phi)_r (u_\phi)_\theta] \\ 2e_{\theta\phi} &= \frac{1}{r} [(u_\phi)_\theta - u_\phi \cot \theta + (u_\theta)_\phi / \sin \theta] - \frac{1}{r^2 \sin \theta} [A\phi + BD + E(u_\phi)_\theta] \\ 2e_{\phi r} &= \frac{1}{r} [r(u_\phi)_r - u_\phi + (u_r)_\phi / \sin \theta] - \frac{1}{r \sin \theta} [C(u_r)_r + D(u_\theta)_r + E(u_\phi)_r] \end{aligned} \quad (2.5)$$

where $A = (u_r)_\theta - u_\theta$; $B = (u_\theta)_\theta + u_r$

$C = (u_r)_\phi - u_\phi \sin \theta$; $D = (u_\theta)_\phi - u_\phi \cos \theta$

$E = (u_\phi)_\phi + u_r \sin \theta + u_\theta \cos \theta$

where $(u_r)_r = \frac{d}{dr} (u_r)$; $(u_r)_\theta = \frac{d}{d\theta} (u_r)$; $(u_r)_\phi = \frac{d}{d\phi} (u_r)$ etc.

If we neglect the squares and products of the displacements and their derivatives in 2.5), we get the infinitesimal components of strain.

3. BENDING OF A CIRCULAR PLATE INTO A SPHERICAL SHELL

Suppose that in the undeformed state of the body, it is a circular plate bounded by the planes $x_3 = a_1$, $x_3 = a_2$, $a_2 > a_1$, and the cylinder $x_1^2 + x_2^2 = a^2$. The plate is then bent into a part of a spherical shell of outer radius r_2 and inner radius r_1 and the edge $\theta = \alpha$, by applying a couple to the edge only. Let y_i axes coincide with x_i axes and the curvilinear coordinates θ_i in the deformed state be a system of polar coordinate (r, θ, ϕ) so that $y_1 = r \sin \theta \cos \phi$, $y_2 = r \sin \theta \sin \phi$, $y_3 = r \cos \theta$ (3.1)

Since the deformation is symmetrical about the x_3 - axis we see that

- (i) the planes $x_3 = \text{constant}$, in the undeformed state, become the spherical surfaces $r = \text{constant}$ in the deformed state.
- (ii) the curves $x_1^2 + x_2^2 = \text{constant}$, in the undeformed state, become the small circles $\theta = \text{constant}$ in the deformed state.
- (iii) $\tan^{-1}(x_2/x_1) = \phi$

(3.2)

These imply that $x_3 = f(r)$, $(x_1^2 + x_2^2)^{1/2} = F(\theta)$

(3.3)

Components of strain and stress-strain relations

From (3.2) we get

$$x_1 = F(\theta) \cos \phi, x_2 = F(\theta) \sin \phi \text{ and } x_3 = f(r) \quad (3.4)$$

Then the finite displacements in cartesian coordinates are given by

$$\begin{aligned} u_1 &= y_1 - x_1 = y_1 - F(\theta) \cos \phi \\ u_2 &= y_2 - x_2 = y_2 - F(\theta) \sin \phi \\ u_3 &= y_3 - x_3 = y_3 - f(r) \end{aligned}$$

In polar coordinates these transform into

$$\begin{aligned} u_r &= r - f \cos \theta - F \sin \theta \\ u_\theta &= f \sin \theta - F \cos \theta \\ u_\phi &= 0 \end{aligned} \quad (3.5)$$

Substituting (3.5) in (2.5), we get the strain components in polar coordinates as

$$\begin{aligned} 2e_{rr} &= (1 - f'^2) \\ 2e_{\theta\theta} &= (1 - F'^2/r^2) \\ 2e_{\phi\phi} &= (1 - F'^2/r^2 \sin^2 \theta) \\ e_{r\theta} &= e_{\theta\phi} = e_{\phi r} = 0 \end{aligned} \quad (3.6)$$

where $f' = \frac{df}{dr}$ and $F' = \frac{dF}{d\theta}$.

Substituting (3.6) in (1.1), the stress-strain relations are given by

$$\begin{aligned} t_{rr} &= \lambda I + \mu (1 - f'^2) \\ t_{\theta\theta} &= \lambda I + \mu (1 - F'^2/r^2) \\ t_{\phi\phi} &= \lambda I + \mu (1 - F^2/r^2 \sin^2 \theta) \\ t_{r\theta} &= t_{\theta\phi} = t_{\phi r} = 0 \end{aligned} \quad (3.7)$$

$$\text{where } 2I = 3 - f'^2 - \frac{1}{r^2} (F'^2 + F^2 / \sin^2 \theta)$$

Equations of equilibrium

The first and second equations of equilibrium give

$$\frac{\partial t_{rr}}{\partial r} + (2t_{rr} - t_{\theta\theta} - t_{\phi\phi})/r = 0 \quad (3.8)$$

$$\frac{\partial t_{\theta\theta}}{\partial \theta} + (t_{\theta\theta} - t_{\phi\phi}) \cot \theta = 0 \quad (3.9)$$

$$\text{which give } \left(\frac{\lambda}{2} + \mu \right) r^3 \frac{df'^2}{dr} + 2\mu r^2 f'^2 = (\lambda + \mu) (F'^2 + F^2 / \sin^2 \theta) \quad (3.10)$$

$$\lambda \frac{d}{d\theta} (F'^2 + F^2 / \sin^2 \theta) + 2\mu \frac{dF}{d\theta} = 2\mu (F^2 / \sin^2 \theta - F'^2) \cot \theta \quad (3.11)$$

and the third is identically satisfied.

As the left hand side and the right hand side of the equation (3.10) are functions of r and θ respectively, we get

$$\left(\frac{\lambda}{2} + \mu \right) r^3 \frac{df'^2}{dr} + 2\mu r^2 f'^2 = c_0^2 (\lambda + \mu) \quad (3.12)$$

$$F'^2 + F^2 / \sin^2 \theta = c_0^2 \quad (3.13)$$

where c_0^2 is an arbitrary constant.

$$\text{Solving (3.12) we get } f'^2 = \frac{c_1^2}{r^{2c}} - \frac{c_0^2 (2 - c)}{2(1 - c)r^2} \quad (3.14)$$

whose solution is

$$= \frac{c_1}{1 - c} \left[(r^{2-2c} - k^2)^{1/2} - k \tan^{-1} (r^{2-2c} - k^2)^{1/2} / k \right] + c_1 \quad (3.15)$$

where c_1^2 and c_2 are arbitrary constants, and

$$c = 2\mu / (\lambda + 2\mu), 0 < c < 1 \text{ and } k = \frac{(2-c)c_0^2}{2(1-c)c_1^2} \quad (3.16)$$

We have to find $F(\theta)$ satisfying (3.11) and (3.13). The equation (3.11) reduces after substitution from (3.13) to

$$\frac{dF'^2}{d\theta} + 2F'^2 \cot \theta = c_0^2 \cot \theta \quad (3.17)$$

$$\text{which gives } F'^2 = c_0^2/2 + c_3/\sin^2 \theta$$

where c_3 is an arbitrary constant.

Since F'^2 becomes infinite at $\theta = 0$, we must take $c_3 = 0$, so that

$$F'^2 = c_0^2/2 \quad (3.18)$$

Hence, since the boundary is symmetrical with respect to the origin we have

$$F = c_0 \theta / \sqrt{2} \quad (3.19)$$

substituting (3.18) and (3.19) in (3.13) we get

$$\theta / \sin \theta = 1, \text{ i.e. } \theta / (\theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \dots) = 1 \quad (3.20)$$

The equation (3.20) is a necessary condition for the consistency of the equations (3.11) and (3.13) satisfied by $F(\theta)$. It is satisfied only when the maximum value of θ (= radius of the circular plate in the strained state / the radius of the spherical shell), measured in radians, is so small that θ^3 can be neglected when compared to θ . This, however, will give a fairly good result upto $\theta = 30^\circ$ ($= 0.5236$ radians), because in this case $\theta / \sin \theta = 1.0472$, involving an error of less than five per cent.

Stresses and Displacements.

Substituting (3.13) (3.18) and (3.19) in (3.7), we get

$$t_{rr} = \frac{\mu}{c} \left[(3 - 2c) - \frac{c_1^2}{r^2 c} + \frac{(3 - 2c)c c_0^2}{2(1 - c)r^2} \right] \quad (3.21)$$

$$t_{\theta\theta} = t_{\phi\phi} = \frac{\mu}{c} \left[(3 - 2c) - \frac{(1 - c)c_1^2}{r^2 c} \right] \quad (3.22)$$

Substituting (3.15) and (3.19) in (3.5) we get the non-vanishing displacements

$$\begin{aligned} u_r &= r - \frac{c_1}{1-c} \left[(r^2 - 2c - k^2)^{1/2} - k \tan^{-1} (r^2 - 2c - k^2)^{1/2} / k \right] - \frac{c}{o} \theta^{2/\sqrt{2}} - c_2 \\ u_\theta &= \left\{ \frac{c_1}{1-c} \left[(r^2 - 2c - k^2)^{1/2} - k \tan^{-1} (r^2 - 2c - k^2)^{1/2} / k \right] + c_2 - c_o/\sqrt{2} \right\} \theta \end{aligned} \quad (3.23)$$

If we assume that the point $r = r_1$, $\theta = 0$ (centre of the circular plate) is fixed, we should have

$$u_r = 0, u_\theta = 0 \text{ when } r = r_1 \text{ and } \theta = 0.$$

The second of these equations is identically satisfied and the first gives

$$c_2 = r_1 - \frac{c_1}{1-c} \left[(r_1^2 - 2c - k^2)^{1/2} - k \tan^{-1} (r_1^2 - 2c - k^2)^{1/2} / k \right] \quad (3.24)$$

The constants c_o^2 and c_1^2 are determined from the boundary conditions.

The decrease in the original thickness $2h$ of the plate can be determined if r_1 and r_2 are known. From (3.23) we get

$$\begin{aligned} 2h &= \frac{c_1}{1-c} \left[(r_2^2 - 2c - k^2)^{1/2} - (r_1^2 - 2c - k^2)^{1/2} - k \tan^{-1} (r_2^2 - 2c - k^2)^{1/2} / k \right. \\ &\quad \left. + k \tan^{-1} (r_1^2 - 2c - k^2)^{1/2} / k \right] \end{aligned} \quad (3.25)$$

Boundary conditions.

If the plate is bent by applying forces to the edge only, we should have $i_{rr} = 0$ when $r = r_1$ and $r = r_2$ (3.26)

which give

$$\frac{2c_1^2}{r_1^2} - \frac{(3 - 2c)c_o^2}{(1 - c)r_1^2} = 2(3 - 2c) \quad (3.27)$$

$$\frac{2c_1^2}{r_2^2} - \frac{(3 - 2c)c_o^2}{(1 - c)r_2^2} = 2(3 - 2c) \quad (3.28)$$

By solving these equations we get

$$e_o^2 = 2(1 - c) (r_2^{2c} - r_1^{2c}) (r_1 r_2)^{2-2c} / c (r_2^{2-2c} - r_1^{2-2c}) \quad (3.29)$$

$$e_1^2 = (3 - 2c) (r_2^2 - r_1^2) / (r_2^{2-2c} - r_1^{2-2c}) \quad (3.30)$$

On the edge $\theta = \alpha$, we have $\sin \alpha \int_{r_1}^{r_2} t_{\theta\theta} r dr = 0$

because from the equation of equilibrium (3.8), the equation (3.22) and the boundary conditions (3.26) we have

$$2 \int_{r_1}^{r_2} r t_{\theta\theta} d\theta = \int_{r_1}^{r_2} \frac{\partial}{\partial r} (r^2 t_{rr}) dr = (r^2 t_{rr})_{r_1}^{r_2} = 0$$

Therefore the distribution of tractions on the edge $\theta = \alpha$ give rise to a couple of moment M given by

$$M = \sin \alpha \int_{r_1}^{r_2} t_{\theta\theta} r^2 dr \quad (3.31)$$

which reduces on substitution from (3.22) to

$$M = \frac{\mu}{c} \left[\frac{(3-2c)(r_2^3 - r_1^3)}{3} - \frac{(1-c)e_1^2(r_2^{3-2c} - r_1^{3-2c})}{(3-2c)} \right] \sin \alpha \quad (3.32)$$

Thus we require a couple of moment of M , to keep the plate bent into a spherical surface of inner radius r_1 and outer radius r_2 , the curved surfaces $r = r_1$ and $r = r_2$ being free from tractions. This result obviates the need of an additional force on the edge of the spherical shell required in a previous result (6). Also when $\alpha = 0$, we see that the couple M in (3.28) becomes zero, a result not obtained by Seth (6, 7).

Numerical Examples

(i) for $c = 1/2$, $r_1 = 11$ and $r_2 = 13$, we get

$$e_o^2 = 2r_1 r_2 = 286, \quad e_1^2 = 2(r_1 + r_2) = 48$$

$$3M = \mu (r_2 - r_1)^3 \sin \alpha = 8\mu \sin \alpha \quad (3.33)$$

and the equation (3.25) gives the original thickness of the plate to be

$$2h = 2.25 \quad (3.34)$$

Thus the decreasing in thickness becomes 11 percent.

(ii) for $c = 3/4$, $r_1 = 3$ and $r_2 = 4$, we get

$$\begin{aligned} c_0^2 &= 2 (r_2^{3/2} - r_1^{3/2}) (r_1 r_2)^{1/2} / 3 (r_1^{1/2} - r_1^{1/2}) = 24.155 \\ c_1^2 &= 3 (r_2^2 - r_1^2) / 2 (r_2^{1/2} - r_1^{1/2}) = 39.178 \\ 3M &= 2\mu (r_2^3 - r_1^3) - 13.06 (r_2^{3/2} - r_1^{3/2}) \\ &= 0.63\mu \sin \alpha \end{aligned} \quad (3.35)$$

The original thickness of the plate is found to be

$$2h = 1.03 \quad (3.36)$$

giving the decrease in thickness as 3 per cent.

In (i) and (ii) Seth's result (6) give the decrease in thickness as 27 per cent and 17 per cent respectively. The case of an incompressible plate, which was shown to be physically impossible (6), has been discussed in detail in the following section.

4. INCOMPRESSIBLE PLATE

In the incompressible case $\lambda \rightarrow \infty$ ($c = 0$) and I approaches zero, so that λI has a finite limit (9). Therefore putting $I = 0$ we have

$$f'^2 = 3 - k_0^2 / r^2 \geq 0 \quad (4.1)$$

$$F'^2 + F^2 / \sin^2 \theta = k_0^2 \quad (4.2)$$

where k_0^2 is an arbitrary constant.

Solving (4.1) we get

$$f = \sqrt{3} \left[(r^2 - k_1^2)^{1/2} - k_1 \tan^{-1} (r^2 - k_1^2)^{1/2} / k_1 \right] + k_2 \quad (4.3)$$

where $3k_1^2 = k_0^2$ and k_2 is an arbitrary constant.

$$\text{Now } \lambda I = \frac{\lambda}{2} \left[(3 - f'^2) - \frac{1}{r^2} (F'^2 + F^2 / \sin^2 \theta) \right] \quad (4.4)$$

With the help of (3.10) and (4.1) this can be written as

$$\begin{aligned} I &= \frac{\lambda}{2} \left[3 - f'^2 - \frac{1}{(\lambda + \mu)r^2} \left\{ \frac{(\lambda + 2\mu)r^3}{2} \frac{df'^2}{dr} + 2\mu r^2 f'^2 \right\} \right] \\ &= \frac{\lambda\mu (k_0^2 / 2r^2 - 3)}{(2\mu + \lambda)} \end{aligned}$$

which gives in the limit ($\lambda \rightarrow \infty$)

$$\lambda I = (k_0^2 / 2r^2 - 3) \quad (4.5)$$

As before, for small θ , F is given by

$$F = k_o \theta / \sqrt{2} \quad (4.6)$$

Then the equations corresponding to (3.21) to (3.25) are respectively given by

$$t_{rr} = (3 k_o^2 / 2r^2 - 5) \quad (4.7)$$

$$t_{\theta\theta} = t_{\phi\phi} = -2\mu \quad (4.8)$$

$$u_r = r - \sqrt{3} \left[(r^2 - k_1^2)^{1/2} - k_1 \tan^{-1} (r^2 - k_1^2)^{1/2} / k_1 \right] - k_o \theta^2 / \sqrt{2} - k_2 \quad (4.9)$$

$$u_\theta = \left\{ \sqrt{3} \left[(r^2 - k_1^2)^{1/2} - k_1 \tan^{-1} (r^2 - k_1^2)^{1/2} / k_1 \right] + k_2 - c_o / \sqrt{2} \right\} \theta \quad (4.10)$$

$$k_2 = r_1 \sqrt{3} \left[(r_1^2 - k_1^2)^{1/2} - k_1 \tan^{-1} (r_1^2 - k_1^2)^{1/2} / k_1 \right] \quad (4.11)$$

$$2h = \sqrt{3} \left[(r_2^2 - k_1^2)^{1/2} - (r_1^2 - k_1^2)^{1/2} - k_1 \tan^{-1} (r_2^2 - k_1^2)^{1/2} / k_1 \right. \\ \left. + k_1 \tan^{-1} (r_1^2 - k_1^2)^{1/2} / k_1 \right] \quad (4.12)$$

If the inner surface $r = r_1$ is acted upon by a normal traction $\mu \beta$, where β is a constant, we have $t_{rr} = \mu \beta$ when $r = r_1$, which gives

$$k_o^2 = 2r_1^2 (\beta + 5) / 3 \quad (4.13)$$

$$\text{From (4.1) we should have } k_o^2 \leq 3 r_1^2 \quad (4.14)$$

which on substitution from (4.13) gives

$$\beta \leq -1/2 \quad (4.15)$$

The distribution of tractions on the edge $\theta = \alpha$, give rise to a force F_1 and a couple of moment M_1 given by

$$F_1 = \sin \alpha \int_{r_1}^{r_2} t_{\theta\theta} r dr = -\mu (r_2^2 - r_1^2) \sin \alpha \quad (4.16)$$

$$M_1 = \sin \alpha \int_{r_1}^{r_2} t_{\theta\theta} r^2 dr = -\frac{2\mu (r_2^3 - r_1^3)}{3} \sin \alpha \quad (4.17)$$

On the outer surface $r = r_2$ we have to apply an additional radial force F_2 given by

$$F = \mu \left[\frac{3k_o^3}{2r_2^2} - 5 \right] \quad (4.18)$$

Thus to bend an incompressible circular plate into a spherical shell of inner radius r_1 and outer radius r_2 we require a resultant force F_1 and a couple of moment M_1 on the edge and the radial forces F_2 and $\mu \beta$ on the outer and inner surfaces of the spherical shell respectively.

5. SUMMARY

An exact solution for the problem of finite bending of a circular plate into a spherical shell has been obtained when the ratio of the radius of the circular plate to the radius of the spherical shell is small. It is shown that the plate can be bent by supplying a couple to the edge only. The results have been compared with those obtained previously (6, 7).

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